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(54) **SHEAR THICKENING FLUID CONTAINMENT IN POLYMER COMPOSITES**

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(60) Provisional application No. 60/622,371, filed on Oct. 27, 2004.

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(52) **U.S. Cl.** **428/315.5**; 428/323; 428/304.4; 524/589; 524/612; 524/570; 524/585; 524/582; 524/560; 524/567; 524/556; 524/606; 521/50

(57) **ABSTRACT**

Shear thickening fluid suspoemulsions are shown to exhibit unique material properties that have potential application in a broad range of fields of use. Suspoemulsions containing shear thickening fluids as immiscible blends exhibit a nontrivial shear thickening response for volume fractions as low as 10% of STF in the silicone emulsion. Measurements indicate that the system shows phase inversion and it is even possible to form materials with a cocontinuous microstructure with interesting, hysteretic, shear sensitive behavior. Novel STF containing composites with rubbers are formed by blending the shear thickening fluid within the rubber precursors and then adding the catalyzing agent. It was possible to contain STF in each of the silicones tested and the rubbers exhibited different behavior with incased STF. Shear thickening fluid was added to open cell polyurethane to create a Foam-STF composite which was found to exhibit an significant shear thickening response. Finally, STF composites were also formed by polymer blending, leading to materials with unique and superior performance as a consequence of the STF content and multiphase microstructure.



Pictorial Representation of Emulsion Under Study With Shear Thickening Fluid as Discrete Phase

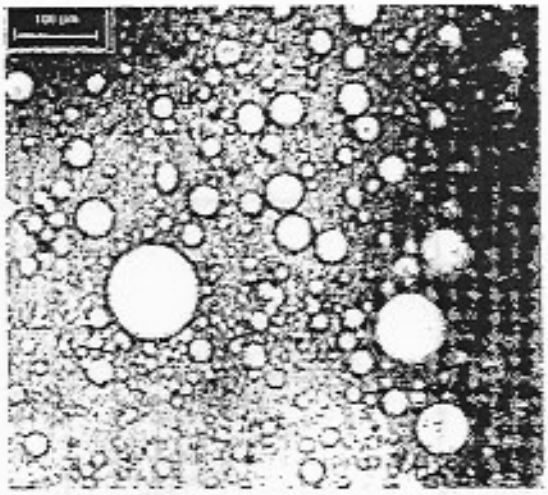


Figure 2a: Droplets of Silicone in Shear Thickening Fluid, $\Phi_{STF} = 63.4$

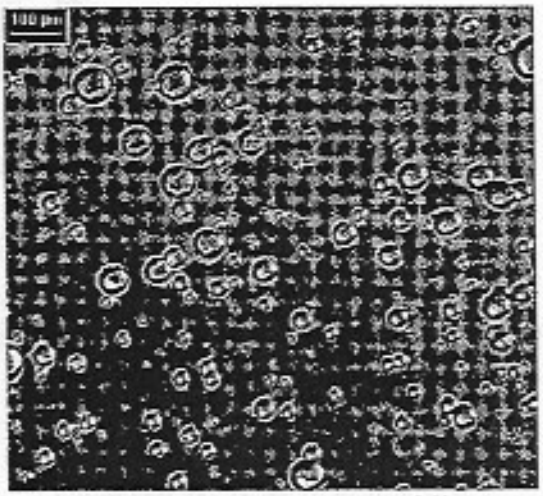


Figure 2b: Droplets of Shear Thickening Fluid in Silicone Oil, $\Phi_{STF} = 10.4$

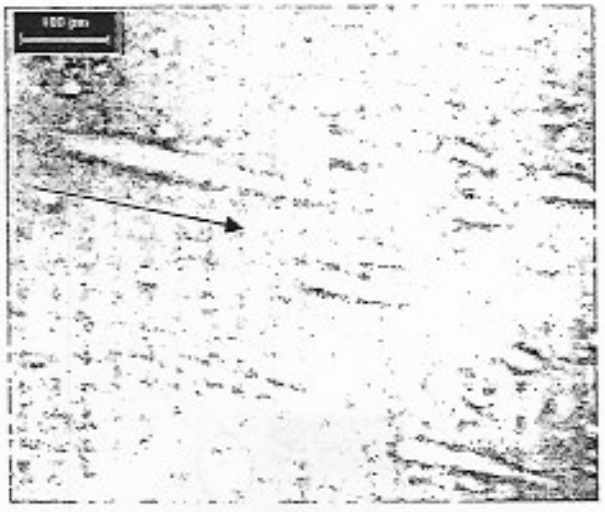


Figure 4a: Silicone Droplets Under Shear, Φ_{STF}=63.4

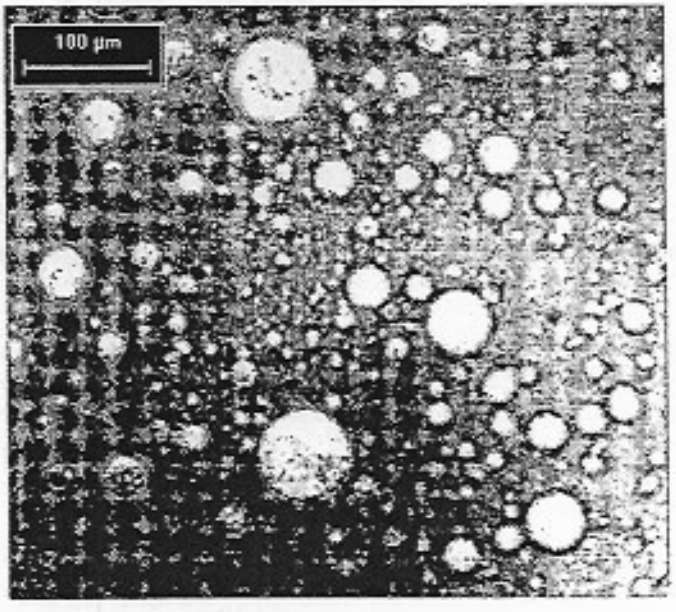


Figure 4b: Silicone in Discrete Phase Shown at Rest, Φ_{STF}=63.4

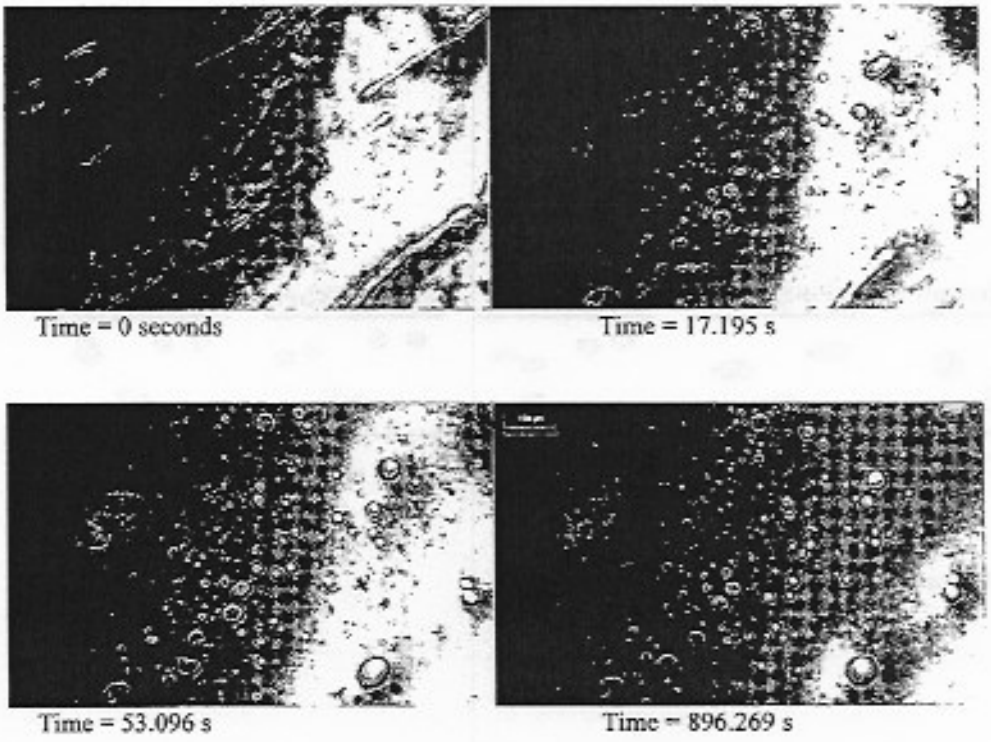


Figure 5: Time Lapse Photographs of STF Suspoemulsionis Subjected to Shear and Allowed to Relax

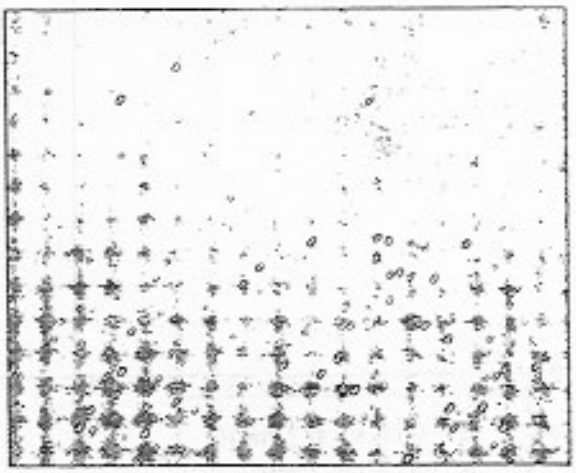


Figure 7a: STF regions in Crosslinked Silicone

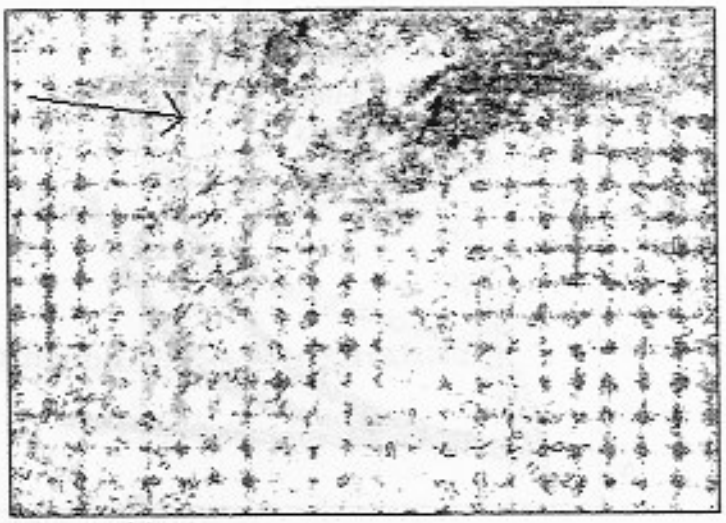


Figure 7b: Ribbed Inclusions of STF

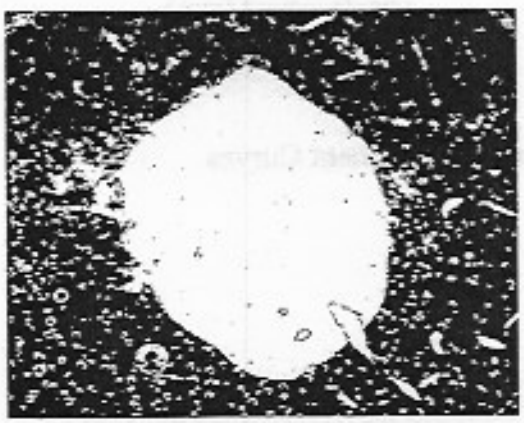


Figure 7c: Shear Thickening Fluid Containment in Silastic T2

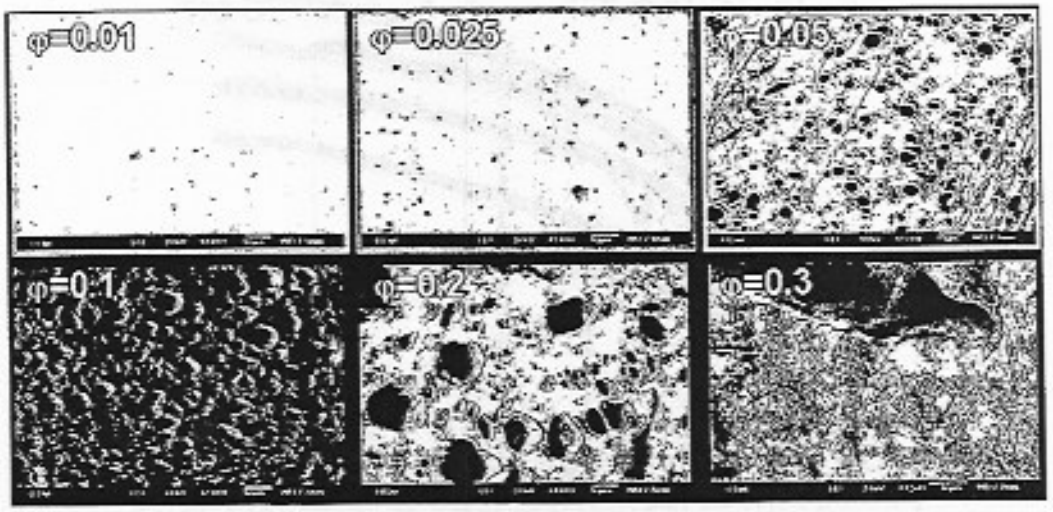


Figure 9. SEM images of STF-PO blend morphology. STF inclusions are evident as holes or particle filled voids, which is a consequence of sample preparation and PEG loss in the electron beam.

SHEAR THICKENING FLUID CONTAINMENT IN POLYMER COMPOSITES

RELATED APPLICATIONS

[0001] This application claims benefit to U.S. application Ser. No. 11/260,742 filed Oct. 27, 2005 and provisional application Ser. No. 60/622,371 filed Oct. 27, 2004 which are incorporated by reference in their entirety for all useful purposes.

BACKGROUND OF THE INVENTION

[0002] Shear thickening fluids (STFs) are fluids whose viscosity increases with shear rate. Of particular interest are discontinuous STFs, which at high shear rates transform into a material with solid-like properties. A typical example of a discontinuous STF is a stabilized suspension of rigid colloidal particles with a high loading fraction of particles. Such systems have been studied for many different combinations of fluid matrix and particle size and compositions (Egres, R. G., Lee, Y. S., Kirkwood, J. E., Kirkwood, K. M., Wetzel, E. D., and Wagner, N. J., "Novel flexible body armor utilizing shear thickening fluid composites." Proceedings of 14th International Conference on Composite Materials. San Diego, Calif. Jul. 14-18, 2003), (Lee, Y. S., Wagner, N. J., "Dynamic properties of shear thickening colloidal suspensions," Rheol Acta 42, 199-208 (2003), (Shenoy, S., Wagner, N. J., Bender, J. W., "E-FiRST: Electric field responsive shear thickening fluids," Rheo Acta 42, 287-294 (2003)). The shear thickening in the colloidal suspension is due to the formation of jamming clusters, or hydroclusters, Lee, Y. S., Wagner, N. J., "Dynamic properties of shear thickening colloidal suspensions." Rheol Acta 42, 199-208 (2003) bound together by hydrodynamic lubrication forces. The hydrocluster growth and collision eventually result in a percolated arrangement of the rigid particles across macroscopic dimension. This microstructural transformation leads to the bulk solid-like behavior. Upon relaxation of the applied stresses, the shear-thickened material typically relaxes to the low strain rate, fluid-like behavior (Eric D. Wetzel, Y. S. Lee, R. G. Egres, K. M. Kirkwood, J. E. Kirkwood, and N. J. Wagner, "The Effect of Rheological Parameters on the Ballistic Properties of Shear Thickening Fluid (STF) KEVLAR®Composites" NUMIFORM, 2004).

[0003] Shear-thickening fluids have been shown to have utility in the fabrication of energy dissipative devices, such as shock absorbers (Hesse, H., U.S. Pat. No. 4,503,952), (Rosenberg, B. L., U.S. Pat. No. 3,833,952), (Sheshimo, K., U.S. Pat. No. 4,759,428) and more recently in the fabrication of ballistic fabric composites (Egres, R. G., Lee, Y. S., Kirkwood, J. E., Kirkwood, K. M., Wetzel, E. D., and Wagner, N. J., "Novel flexible body armor utilizing shear thickening fluid composites." Proceedings of 14th International Conference on Composite Materials. San Diego, Calif. Jul. 14-18, 2003), (Lee, Y. S., Wetzel, E. D., and Wagner, N. J., "The ballistic impact characteristics of KEVLAR® woven fabrics impregnated with a colloidal shear thickening fluid", *J. Mat. Sci.* 38, 2825-2833 (2003), (Eric D. Wetzel, Y. S. Lee, R. G. Egres, K. M. Kirkwood, J. E. Kirkwood, and N. J. Wagner, "The Effect of Rheological Parameters on the Ballistic Properties of Shear Thickening Fluid (STF) KEVLAR® Composites" NUMIFORM, 2004) and puncture resistant materials ("Stab resistance of shear thickening fluid (STF)-treated fabrics" by M. J. Decker, C. J. Halbach, C. H. Nam, N. J. Wagner and E. D. Wetzel, accepted for publication in Composites Science and Technology, August, 2006). There is considerable interest in incorporating STF's into other materials. PCT/US2004/015813 entitled "Advanced Body Armor using a shear thickening fluid" is incorporated by reference in its entirety for all useful purposes. Incorporation of STF's into plastics, rubbers and foams is discussed below. Shear thickening fluids may also contain fillers, see PCT application no. US06/04581 filed Feb. 9, 2006, which is incorporated by reference in its entirety for all useful purposes.

[0004] Within the scope of this invention, the shear thickening fluid is defined as any fluid that exhibits an increase in viscosity with increasing shear rate or applied stress. Shear thickening is not shear dilatancy, which is a material property whereby the material's volume changes upon an applied stress or deformation. Shear thickening fluids, however, may exhibit dilatancy under specific conditions.

[0005] The shear thickening fluids may be concentrated dispersions of particulates within a fluid medium that exhibit an increase in viscosity with increasing applied stress, the particles within the fluid would preferably have a smallest dimension being less than 10 microns, more preferably, less than 1 micron, as well as true nanoparticles being below 100 nm in smallest dimension. Particles can be of any solid material, including spherical amorphous silica such as that produced via Stöber type synthesis, synthetic inorganic particles synthesized via solution precipitation processes such as precipitated calcium carbonate, or synthesized by gel-sol techniques (hematite, TiO2), or fumed silica, or carbon black. Natural inorganic particulates such as montmorillonite and kaolin clays can be dispersed in solvents and have been shown to exhibit shear thickening behavior. Ground mineral powders, such as quartz, calcite, talcs, gypsum, mica can be dispersed in liquid mediums and exhibit shear thickening behavior. The solid dispersed phase can also be polymeric in nature, such as plastisols generated through emulsion polymerization processes such as poly(methyl methacrylate) (PMMA), polystyrene (PS) microspheres such as those available from Polysciences or Bangs Laboratories, Inc. The solid phase can also be starch or other natural polymers.

[0006] There is significant interest in understanding the flow properties and microstructure formation of immiscible blends of liquids. Indeed, the processing and flow of immiscible blends, emulsions, and miniemulsions can affect the microstructure, which can in turn, affect the final material properties. Such blends, emulsions, and miniemulsions occur often in many systems and processes of practical importance. For example immiscible fluids are often used in direct mass contacting operation, such as extraction, while many foods, cosmetics, liquid soaps, and other consumer products are delivered or processed as mixtures of immiscible fluids. Immiscible polymer blends are formulated to achieve physical properties between the limits of the pure components, as well as imparting new characteristics arising from the presence of an interface.

[0007] From a theoretical standpoint the problem has not been solved, as how to describe the immiscible fluid mixtures and so one must rely on experimentation and semi-empirical models for predictions of rheological and material properties. Much work has been done to describe polymer blend systems (Utracki, L. A., "On the viscosity-concentration dependence of immiscible polymer blends," J. Rheol 35(8), 1615-1637 (1991)) so that industrial processing can be streamlined and flow morphology more aptly controlled.

with an immiscible or partially miscible matrix material wherein the STF comprises a solvent and particles suspended in said solvent and the particles are colloidal particles having a particle size less than about 10 microns.

[0016] Another aspect of the invention is drawn to a composite which comprises a suspoemulsion, where the suspension in the suspoemulsion is a shear thickening fluid.

[0017] A further aspect of the invention is drawn to an immiscible blend of a polymer which comprises a polymer with an immiscible or partially miscible shear thickening fluid (STF).

[0018] A further aspect of the invention is drawn to a composite which comprises a shear thickening fluid (STF) in a foam.

BRIEF DESCRIPTION OF THE FIGURES

[0019] FIG. **1** is a pictorial representation of emulsion according to the invention with shear thickening fluid as discrete phase.

[0020] FIG. **2***a* illustrates droplets of silicone in shear thickening fluid, (Φ_{STF}=63.4. FIG. **2***b* illustrates droplets of shear thickening fluid in silicone oil, (Φ_{STF}=10.4

[0021] FIG. **3** illustrates the Viscosity-Shear rate experimental results for the STF, neat silicone fluid, and suspoemulsions.

[0022] FIG. **4***a* illustrates silicone droplets under shear, Φ_{STF}=63.4. FIG. **4***b* illustrates silicone in discrete phase shown at rest, Φ_{STF}=63.4. FIG. **4**c illustrates silicone in discrete phase under shear, Φ_{STF}=63.4, displaying droplet deformation.

[0023] FIG. **5** illustrates time lapse photographs of sample subjected to shear and allowed to relax.

[0024] FIG. **6** illustrates stress-time droplet evolution.

[0025] FIG. **7***a* illustrates the discrete regions of STF formed in the silicone can be observed in a sample 18% mass STF. FIG. **7***b* shows the ribs of shear thickening fluid formed in Silastic T2 (28% mass STF), highlighted with an arrow, upon curing. FIG. **7***c* shows a large droplet of shear thickening fluid (white area) that was contained inside of a cured Silastic T2 silicone sample.

[0026] FIG. **8** shows the results of compression testing of neat Foam and STF-foam composites for various rates of deformation.

[0027] FIG. **9** shows micrographs of the phase morphology in STF polymer composites obtained by scanning electron microscopy.

[0028] FIG. **10** shows ASTM Trouser Tear Test Results for STF-PO samples.

DETAILED DESCRIPTION OF THE INVENTION

[0029] We show novel materials formed from shear thickening fluids in scaffolds, such as foams. We determined the rheological properties of an emulsion containing a shear thickening fluid immiscibly blended with silicone oil, forming a novel shear thickening suspoemulsion. The system is also hypothesized to follow standard shear droplet morphology, with competition between coalescence and breakup. We also formed such shear thickening suspoemulsions using STFs blended with melted polymer, such that upon cooling, the novel microstructures formed during processing were "frozen" in upon solidification. The latter yielded materials comprising encapsulated shear thickening fluids with greatly enhanced material properties.

[0030] Solid-Shear Thickening Fluid Composites

[0031] One method comprises STFs in scaffold materials. Such scaffold materials would include, but are not limited to, open cell foams, such as those produced from polyurethanes, polyolefins or any polymeric material. Another porous scaffold material that would have utility is expanded polytetrafluoroethylene (ePTFE) such as found in several materials sold under the trade name GORE-TEX® (W. L. Gore and Associates, Inc.), or microporous or expanded polyethylene. Another scaffold material would be an engineered porous plastic or rubber, where inclusions are available to be filled partly or completely with STF.

[0032] Another type of scaffold material would include porous natural materials, including but not limited to wood, porous stone such as sandstone, pumice etc., and the skeletons of marine organisms including corals and sponges.

[0033] Alternatively, the scaffold material could be a building material such as concrete or asphalt. The presence of shear thickening fluid could absorb damaging impact energy within these materials which contribute to fatigue failure or catastrophic failure of articles made therefrom.

[0034] A second method by which a rubbery or solid (referred to herein as the second material)-shear thickening fluid composite containing discrete or co-continuous regions of shear thickening fluids, such as a suspoemulsion, can be fabricated is via mixing STF with an immiscible or partially immiscible liquid or fluid-like component (such as a molten polymer, or resin that can be foamed or crosslinked) that can subsequently be converted to a solid through heating, cooling, chemical reaction, etc. Candidate materials would preferably exhibit little solubility with the liquid suspending medium used to generate the shear thickening fluid, at least on the time scales and at the processing conditions required to transition the material from a liquid to a solid. Control of the morphology can be tuned based on choice of shear thickening fluid and second material liquid component, the relative compositions of the STF and second material liquid component, shear or processing conditions, and the addition of process adjuvants such as surfactants, fillers, block copolymers, nano and colloidal particles, such as used in pickering emulsions, and the like.

[0035] One type of second material would include reactive polymeric materials that cure or crosslink to form solids. Reactive polymers include polyurethanes that cure through the chemical reaction of components (polyols and isocyanates), epoxies that cure through the addition of a catalyst, and UV curable resins. A preferred second material of this type would be from the class of elastomeric or elastomeric gel materials, such as silicone rubber (cross-linked PDMS) or silicone gels and the like, which can be relatively low viscosity liquids prior to cross-linking, whereafter they form resilient materials with good rebound characteristics. A variety of elastomers exist to provide a wide range of properties such as chemical and solvent resistance, temperature resistance, and hardness (durometer). These materials could be mixed with shear thickening fluids at room temperature to disperse the shear thickening fluids adequately and to achieve the desired composite morphology or shear thickening fluid droplet size. The liquid-like second material could subsequently be cured, or the curing could be accelerated through heating or the addition of additional components that catalyze the reaction and transform the second material into a solid.

[0036] Another type of second materials would include melt processable polymers or thermoplastic elastomers

material could be incorporated into gloves that can serve to reduce vibration or protect the hands from a jarring impact. One possible application would be the wrist protection guards worn during roller skating and roller blading. Additionally, such conformable padding could be used to generate knee pads, elbow pads and the like for providing improved safety from impact to specific regions. The padding can be used in any other sport that requires padding, such as but not limited to baseball, football, hockey, lacrosse, fencing. Besides gloves, elbow and knee pads, other examples of uses of the padding include but are not limited to shin guards, shoulder pads, leg pads, chest protectors, and athletic cups.

[0049] A conformable cast material can be fabricated from the polymeric or elastomeric-shear thickening fluid composites containing discrete droplets, or co-continuous regions of shear thickening fluids. Such materials could provide improved protection by limiting movement (twisting, bending) of a broken bone, muscle strain, sprains, or injured limb (wrist, elbow, ankle, knee, neck, spine or the like. Such a material could also be used as a cast material worn while strains and sprains are healing similar to air casts to the ankle, wrist or the like which allows movement but protects against rapid twisting or impacts which could re-injure the region. Such materials can be of application in orthopedic applications, where protection from fall and impact of hips, knee and elbow and other joints is desired.

[0050] The novel conformable composite comprised of discrete droplets, or co-continuous networks of shear thickening fluids could be used in seat cushioning and neck supports in automobiles, airplanes, trains and the like to provide more protection during accidents. This would be particularly beneficial for protecting the spine and neck from injury such as from torque or whiplash.

[0051] Pads fabricated of conformable and resilient composites containing shear thickening fluids as discrete droplets or co-continuous networks within a plastic or elastomer second material could be positioned at high stress and/or frequently impacted regions such as beneath the heel and beneath the ball of the foot. The nature of the fluid within these types of pads could also be a large pocket of fluid directly local to the point of impact or potential point of impact. These pads could be incorporated directly into a sports shoe design or as part of a shoe insert to reduce impact during walking, running, jumping and the like. The pads can be used as an orthotic placed in the shoe. A potential energy dissipative construction for an athletic shoe would allow shear thickening fluid to pass through channels connecting pockets located beneath the ball of the foot and heel, allowing transfer of shear thickening fluid between both impact regions as a result of the natural heel-to-toe weight transfer associated with walking, running and the like. Such materials can be of military application in boots such as but not limited to para-trooper boots.

[0052] Mechanical components could be fabricated from solid materials containing shear thickening fluids as discrete droplets or regions or as a co-continuous network within the solid material. Smart components could be fabricated where the stiffness or hardness of a flexible component can change as a result of degree of deformation, such as from elongation, bending, torque, twisting, compression, or dependent on the rate of elongation, bending, torque, twisting, compression. Such components could have utility as part of a suspension which could stiffen in response to bending, etc.

[0053] The novel blends of shear thickening fluids and a second liquid material discussed earlier could have utility in several applications used as a medium to control mechanical actuation of one object relative to another. This material could be used as a shock absorbing medium, such as within the rotary shock absorber discussed by Hesse, U.S. Pat. No. 4,503,952, the viscoelastic damper discussed by Seshimo (U.S. Pat. No. 4,759,428), or the tug resistant link discussed by McMahon et al. (U.S. Pat. No. 5,712,011). Additionally, the novel energy dissipative blend could be used to control, attenuate, or facilitate the transfer of energy between two or more objects such as that associated with torque, translation and vibration. These novel composites could be used in hard drive and CD drive vibration or shock dissipation, or to protect from impact sensitive mechanical, electrical, or optical equipment.

EXAMPLES

Example 1

Shear Thickening Suspoemulsion

[0054] FIG. **1** illustrates a representation of the suspoemulsions with shear thickening fluid (STF) as the dispersed phase

[0055] STF-Suspoemulsion Preparation: The first part of the two-part emulsion is a shear thickening fluid (STF) which comprises polyethylene glycol and silica particles. The fluid was prepared using amorphous silica powder with an average particle diameter of 450 nm (Nippon Shokubai KE-P50) dispersed in 200 MW Polyethylene Glycol (Clariant PEG-200), Table 1. The silica particles were first added to PEG at a weight fraction of 30% with the dilutteness of the system aiding in particle dispersion. This mixture was then centrifuged for 2 hours and the supernatant removed, leaving a cake of close packed silica particles (Φ~64%). Very small amounts of PEG were added to the silica particles until the mixture reached the desired flow properties, higher additions of PEG at this stage would decrease the viscosity of the solution. PEG can be easily replaced by lower molecular weight solvents, such as ethylene glycol. Thermogravimetric analysis was conducted on the sample to determine the weight fraction of particles in this final solution, 59.52%, which was then used to determine the volume fraction of silica in PEG. All emulsions were formulated with the same 49 vol % silica shear thickening fluid.

TABLE 1

	Material Properties	
	ρ (g/cm3)	η_s (Pa·s)
Silica	2.055	—
PEG	1.02	0.057
Silicone Part A	1.12	21.4

[0056] The second part was a silicone oil, acquired from GE Silicones (SLE5700-D1), and was chosen for its Newtonian viscosity behavior and high immiscibility in PEG. For the rheological testing only Part A of the two part polymerizable silicone was used. The silicone can be polymerized with the addition of the catalyzing agent, Part B.

[0057] The emulsions were prepared by weighing out a specific mass of each fluid in a 20 mL glass scintillation vial and then mixing by hand with a spatula. The samples studied are given in Table 2, with a wide compositional range. The

TABLE 4-continued

Viscosity of Suspoemulsions as a Function of Stress and STF Phase Volume

	Stress vs. STF Phase Volume%					
	0%	15.87%	36.55%	55.14%	82.86%	100%
5 Pa	21.475	45.417	106.460	154.690	3132.300	238.770
10 Pa	21.603	42.415	88.743	38.891	327.510	26.232
30 Pa	21.591	38.188	61.566	13.736	31.966	9.2456
100 Pa	21.599	33.417	44.886	19.923	64.788	33.087

[0068] Once again a behavioral difference is seen as the volume fraction of shear thickening fluid is increased. At low STF loadings the effects of shear stress on viscosity are minimal, whereas at higher STF loadings, the nonlinear dependence of the STF component is evident in the emulsion viscosity.

[0069] Dynamic tests were run for all samples at both one and five radians per second so that the linear viscoelastic region could be determined. This is described in greater detail in U.S. application Ser. No. 11/260,742 filed Oct. 27, 2005, which again is incorporated by reference in its entirety including all the figures. The low STF loading samples show minimal effects of increasing stress amplitudes, whereas the high STF loading emulsions show non-linear behavior typical for the STF component (Lee, Y. S., Wagner, N. J., "Dynamic properties of shear thickening colloidal suspensions," Rheol Acta 42, 199-208 (2003)). There are seemingly few differences between the responses of the mixtures at the two different frequencies tested. The viscous contribution is seen to be an order of magnitude greater at the high frequency where as the elastic contribution is on the same order for both frequencies.

[0070] STF-Suspoemulsion Structure by Optical Microscopy: The samples were imaged to determine the continuous and discrete phases formed in emulsions with varied shear thickening fluid compositions. As shown in FIGS. **2***a* and **2***b* it was possible to create discrete phases of each component in a continuous phase of the other. An analysis of the response of the emulsions to shear was performed using the shear cell constructed of glass slides. A small amount of sample was plated between two glass slides allowing shear of the sample by movement of either slide while fixing the other. The shearing between plates was done by hand. The setup permits one to view in a direction perpendicular to the flow field.

[0071] FIG. **4***a* shows a sample with Φ_{STF}=63.4 under a stress that is not known, an arrow is added to indicate the direction of shear. What can be seen is the elongation of the silicone droplets under this shearing action. FIG. **4***b* shows this same sample at rest and again under shear in **4**c, establishing that the STF inclusions remain in a flowable form inside the suspoemulsion.

[0072] To further investigate whether the STF suspoemulsion can relax after deformation and shear thickening, a sample consisting mostly of shear thickening fluid, Φ_{STF}=63.4, was plated on top of a single glass slide (no cover) and subjected to a shear stress at t>0. Once the stress was removed the state of the system was recorded using image-capturing software on the microscope. This is shown in FIG. **5**, with silicone occupying the discrete regions in a continuous shear thickening fluid matrix. The time stamps of when the pictures were taken are given and could be used to calculate the surface tension between the phases. Evident from the slides is the elongation of the discrete phases of silicone and the subsequent relaxation back into a spherical shape. Some of the elongated threads are observed to break into droplets. This overall behavior is expected as a lower energy state is reached with a decreased interfacial area and is in agreement with the predictions of Edwards, B. J., Dressler, M., "A rheological model with constant approximate volume for immiscible blends of ellipsoidal droplets," Rheol. Acta 42, 326-337 (2003).

[0073] STF Suspoemulsion Discussion of Results

[0074] The rheological behavior of the emulsions is interesting as discrete phases of a shear thickening fluid are shown to influence the flow properties of a Newtonian fluid matrix at low concentrations of shear thickening fluid. The nature of the experimental method does not allow for visual confirmation of microstructure under shear, as would be possible in a glass Couette cell (Rusu, D., Peuvrel-Disdier, E., "In situ characterization by small angle light scattering of the shear-induced coalescence mechanisms in immiscible polymer blends," J. Rheol. 43(6), 1391-1409 (1999)). However, through simple analysis of the rheological behavior and pictures of the system at steady state an understanding of the structure and continuity of the system can be developed. Analysis can begin keeping in mind the key results of FIGS. **2***a* and **2***b*. FIG. **2***a* shows that when small amounts of silicone are added to the shear thickening fluid discrete regions of silicone are formed. The same is true for small amounts of shear thickening fluid added to silicone, FIG. **2***b*. It is then hypothesized that there is a phase inversion between a continuous phase of shear thickening fluid and a continuous phase of silicone at some intermediate volume fraction of shear thickening fluid.

[0075] FIG. **3** displays the viscosity stress relationships of the emulsions and clearly shows the shear thickening behavior for each emulsion tested with flow curve characteristics dependent on volume fraction of shear thickening fluid. The discontinuous shear thickening observed in pure shear thickening fluid is also observed in the samples with a volume fraction of fifty-six percent shear thickening fluid. As the amount of shear thickening fluid decreases, the behavior changes as the fluids display a shear thickening transition followed by a second region of shear thinning at higher shear rates, FIG. **3**. These results partially confirm the hypothesis that samples with shear thickening fluid in the continuous phase will exhibit discontinuous shear thickening while samples with shear thickening fluid in the discrete phase will not. It is also evident that there is a different response for emulsions around the region where shear thickening fluid is half of the mixture by mass (Φ_{STF}=37.5). Also apparent is the change in shear thinning behavior for samples as the volume of shear thickening fluid is lowered, from a very steep and drastic shear thinning regime to a flatter, more Newtonian like fluid behavior.

[0076] The dynamic rheological testing of the emulsion can also be used to extract behavior differences between samples. Analysis of the loss modulus shows that for the samples with Φ_{STF}>37.5 there is a very steep shear thickening transition with increasing stress amplitude. In the sample where Φ_{STF}≤37.5 the shear thickening response is characteristically different and subdued from the pure shear thickening fluid. This response difference suggests that when that sample is at rest, as in small amplitude dynamic testing, the shear thickening response is different from the response under steady shear. The shear thickening response in the shear test-

[0088] A two part room temperature foam was acquired from Quantum Foam Resins, LDF 8, with a mix ratio of 100:7. The density of the first part is ρ_{STF_A}=1.2 gm/cm^3 and plays an important part in the suspension of the shear thickening fluid, ρ_{STF}=1.67 gm/cm^3. If the density ratio were too large the settling time of the shear thickening fluid would be on a time scale less than that of the curing process. A florescent dye (DayGlo Color Corp, D-824) was added to the shear thickening fluid to aid in visual recognition of shear thickening inclusions. The following foam compositions were formed, Table 17.

TABLE 5

Closed Cell Foam Compositions, Quantum Foam Resins LDF 8

Φ_{STF}	Part A (gm)	Part B (gm)	Mass of Shear Thickening Fluid (gm)
0	4.0528	0.3226	0
10	3.5655	0.2427	0.5351
25	3.0468	0.2051	1.4597
50	2.0814	0.1446	2.8718

[0089] Testing: Controlled Compression: The response of the materials to a controlled compression between two parallel plates was tested. The compression was done between two parallel plates on a rheometer (25 mm Parallel Plate, Paar Physica MCR500) using the analog of an adhesive tack test. The velocity of the upper plate was controlled and the resulting force load recorded. The velocities were measured from 0.1 mm/s to 5 mm/s.

[0090] The tests were performed on foam samples (Table 6) cut into a 25 mm diameter circle with a thickness of 0.25 inch. The shear thickening fluid was added to the foam until the shear thickening response could be felt throughout the foam with pressure applied between fingers. The amount of shear thickening fluid in the foam composite is less than the porosity of the foam, and there is air inside of the foam-STF composite.

TABLE 6

Polyurethane Based Open Cell Foam Composites

Sample	Mass Foam (gm)	Mass STF (gm)
1	0.1773	0
2	0.1743	7.3557
3	0.1771	8.4029

[0091] Drop Testing: A ¾ inch diameter spherical ball bearing with a mass of 28.81 grams was used for impact testing. The impact was recorded using a digital camera. Impact testing was performed on the polyurethane based open cell foams with the compositions given in Table 6. The spherical ball bearing was dropped onto the target by hand from an approximate distance of one foot. The results were recorded using a digital camera (Sony P51) in quick snap mode exposing thirty frames per second.

[0092] Silicone Rubbers: The ability to encapsulate shear thickening fluid inside of the polymer matrix was studied by mixing quantified amounts of shear thickening fluid with the silicone precursors. For all silicone rubbers tested the shear thickening fluid was easily mixed into the precursor. In FIG. 7*a* the discrete regions of STF formed in the silicone can be observed in a sample 18% mass STF. FIG. 7*b* shows the ribs of shear thickening fluid formed in Silastic T2 (28% mass STF), highlighted with an arrow, upon curing.

[0093] FIG. 7*c* shows a large droplet of shear thickening fluid (white area) that was contained inside of a cured Silastic T2 silicone sample. Close observation of the shear thickening fluid displays cracks due to fracturing of the fluid when the rubber was stretched. These fissures disappear once the fluid has relaxed. There are many air bubbles contained within the cured rubber and this problem could be alleviated with the use of a vacuum chamber prior to curing the sample.

[0094] When the rubber sample shown in FIG. 8*c* is stretched the region of shear thickening fluid visually changes from translucent to opaque. When fully relaxed the index of refraction of the shear thickening fluid is closely matched with that of the silicone and the droplet appears translucent. When a strain is applied to the sample the shear thickening fluid hardens, and turns into a region of opaqueness. If a large enough strain is applied the fluid can be torn apart and fissures such as shown above are readily formed. When the strain is removed the fluid relaxes back to its original translucent state.

[0095] Open Cell Foam: Shear thickening fluid was added to the open cell foams and found to wet very well. The shear thickening response of the shear thickening fluid in the open cell foam is observable by hand in both foams with large and small pores (60-100 parts per inch (ppi)). The reaction of the material is that of the neat fluid. At fast impact speeds the foam appears to act like a solid and at low strain rates the composite can be easily compressed and the fluid is seen to flow out of the pores. This was further quantified with the impact testing shown later.

[0096] Closed Cell Foam: The addition of shear thickening fluid to the closed cell foam was found to inhibit the catalyzing agent used to foam and cure the resin. It formed a goop similar in consistency to baking dough. Even addition of twice as much catalyzing agent to the mixture does not allow the curing of the foam. We anticipate the successful incorporation of STF into the closed cell foam through the use of a catalyst that is not inhibited by the STF.

[0097] Dynamic Testing of Foam STF Composites: Upon slow compression of open cell foams containing STF at stresses between the plates below critical stress of shear thickening, the fluid was found to flow out of the foam and collect at the base. Upon retraction of the upper plate to the original position some of the fluid would be wicked into the foam, however not all was taken into the pores.

[0098] Dynamic tests were performed on closed cell foam composites with results reported in U.S. application Ser. No. 11/260,742 filed Oct. 27, 2005, which again is incorporated by reference in its entirety including all the figures. Analysis of the dynamic properties of a similar shear thickening fluid can be found in Lee and Wagner (Lee, Y. S., Wagner, N. J., "Dynamic properties of shear thickening colloidal suspensions," Rheol Acta 42, 199-208 (2003)). There was a large amount of slip occurring at the plate-foam interface at high rotation angles. The amount of slip was not quantified but could be eliminated if the foam were to be attached to the plates using an adhesive. Foam was observed to fail mechanically at high stresses. However, for the STF-Foam composite there is a shear thickening effect observed at high stress, such that the STF-Foam composite was observed to increase in both elasticity and viscosity, in contrast to the Foam itself. It

TABLE 8-continued

Energy dissipation during Tear Tests

Volume Fraction of STF Phase	Energy Dissipated During Tear Test (J)
0.3	0.06
0.01	0.64
0.025	0.83

[0113] Blends with 5 vol % STF dissipate the highest energy during this test, and this value is more than 3 times higher than the neat polyolefin.

[0114] Table 9 displays the maximum load achieved and the maximum extension.

TABLE 9

Tear Testing Results for Maximum Load and Maximum Extension

Volume Fraction of STF Phase	Maximum Load (N)	Extension at Maximum Load (m)
0.01	5.3	0.1568
0.025	5.4	0.2033
0.05	6.3	0.2073
0.1	5.9	0.2068
0.2	4.6	0.208
0.3	1.8	0.0642

[0115] The latter is limited by the instrument to 0.2 meters, and so the true maximum extension achievable is at least this high if not higher for the STF-PO blends that do not fracture. The maximum load achieved is for the 5 vol % STF-PO blend, and the maximum extension is reached already for the 2.5 vol % blend. The presence of STF inclusions increases the maximum load by over 20% and the maximum extension to >75% above the performance of the neat PO.

[0116] ASTM D 882 tensile elongation tests were performed using the miniInstron with serrated grip faces at an initial grip separation of 50 mm and an elongation rate of 250 mm/min. The results, shown in Table 10 shows that the 1 vol % STF-P0 blend has the highest shear modulus and the 10% STF-P0 blend has the Young's modulus.

TABLE 10

Elastic Shear Modulus G' and Young's Modulus of STF-PO blends.

Volume Fraction of STF Phase	G' (100 Rad/s) (MPa)	Young's Modulus (MPa)
0	4.7	
0.01	4.78	
0.025	4.33	
0.05	3.87	6.07
0.1	3.5	7.11
0.2	3.65	5.24
0.3	3.45	

[0117] Further, the neat PO, not shown, fails at the grip and does not extend. This is further evidence of the strengthening and toughening effect of the STF inclusions during deformation of the PO blends.

SUMMARY

[0118] We have demonstrated a novel composite material comprised of a shear thickening fluid (STF) blended or integrated with an immiscible or largely immiscible matrix material. As shown, the matrix material can be a liquid, thus forming a novel suspoemulsion where one phase is shear thickening, which imparts novel rheological behavior. This behavior is a consequence of the STF material's transition at high stresses or shear rates, but also is shown to depend on the state of dispersion of the STF phase. The novel rheology includes a stiffening along with increased rate of energy dissipation at high stresses or shear rates, as observed in both steady, transient, and dynamic oscillatory experiments. The matrix material can also be a foam or crosslinked rubber, where the STF phase is dispersed therein or vice versa. The formation of this composite can be formed by reactive polymerization or crosslinking in the non-STF phase. The matrix material can also be a thermoplastic where the STF is mechanically or otherwise blended into the matrix material while the matrix material is in the molten state, which then solidified upon cooling to the temperature of use. Such novel materials exhibit unique dynamic behavior and show enhancement in mechanical properties and energy absorption upon mechanical impact, as well as enhanced tear resistance and elongational strength.

[0119] All the references described above are incorporated by reference in its entirety for all useful purposes.

[0120] While there is shown and described certain specific structures embodying the invention, it will be manifest to those skilled in the art that various modifications and rearrangements of the parts may be made without departing from the spirit and scope of the underlying inventive concept and that the same is not limited to the particular forms herein shown and described.

1. A composite which comprises a shear thickening fluid (STF) combined with an immiscible or partially miscible matrix material wherein the STF comprises a suspending fluid and particles suspended in said suspending fluid and the particles are colloidal particles having a particle size less than about 10 microns.

2. (canceled)

3. (canceled)

4. (canceled)

5. The composite as claimed in claim **1**, which further exhibits both increased elasticity and/or energy dissipation under shear deformation or applied stress(es).

6. (canceled)

7. (canceled)

8. (canceled)

9. (canceled)

10. The composite as claimed in claim **1**, which further exhibits increased energy dissipation under shear deformation or applied stress(es).

11. The composite as claimed in claim **1**, which further exhibits increased strength under shear deformation or applied stress(es).

12. The composite as claimed in claim **10**, which further exhibits increased strength under shear deformation or applied stress(es).

13. (canceled)

14. (canceled)

15. (canceled)

16. (canceled)

17. (canceled)

18. (canceled)

19. (canceled)

20. (canceled)