Soft Matter

Dynamic Article Links

Cite this: *Soft Matter*, 2012, **8**, 8752

www.rsc.org/softmatter

PAPER

Making an elastomeric composite material *via* the heteroaggregation of a binary colloidal dispersion

Fernando Martínez-Pedrero,†[a] Fanny Alousque,[a] Benoît de Gaudemaris,[b] Julien Berriot,[b] Fabien Gaboriaud,[b] Nicolas Bremond*[a] and Jérôme Bibette[a]

Received 25th February 2012, Accepted 6th June 2012
DOI: 10.1039/c2sm25441g

The incorporation of mineral particles into a polymer matrix leads to extra properties of the polymeric material that are linked to the homogeneity of the mixture. A fine homogeneity can be obtained by using a latex route where the two components are first dispersed in water and then dried. Here, we show a novel way to make an elastomeric composite material *via* a bulk destabilization of a binary colloidal dispersion. The mixture is composed of a natural rubber latex, which is naturally stabilized, and carbon black particles that are dispersed in water with the help of surfactants. We observe either a transition towards a weak gel, which is a reversible state, or a transition towards an irreversible elastic solid. These structural transitions are mainly controlled by the surfactant concentration that tunes the interaction between natural rubber and carbon black particles, the latter bridging polymer droplets together. We also show that the weak gel can become an irreversible elastic solid under a high shear. This shear-induced heteroaggregation phenomenon exhibits the features of a thermally activated process.

1 Introduction

The embedding of solid particles in polymer matrices is a widespread procedure for improving mechanical properties of elastomeric materials[1] as well as for designing conductive composite materials.[2] The final properties of the composite are a function of the surface chemical properties of the dispersed phase, through the filler–matrix and filler–filler interactions, and structural factors such as size distribution and shape of the filler, including its fractal feature and its spatial distribution in the host matrix.[3,4] One of the most challenging tasks while processing such materials is the ability to homogeneously disperse the filler component since the macroscopic features of the composites are intrinsically linked to their microscopic architecture.[5] Therefore, several strategies have been designed for controlling the filler distribution into the matrix.[6] Solid particles can be dispersed into the polymer matrix by direct melt compounding. Another approach is to use a solvent for reducing the continuous phase viscosity or to tune the interactions at the filler–polymer interfaces through functionalization of the filler surface or modification of the polymer matrix. The filler can also be incorporated before polymerisation and formation of the matrix or by being created *in situ.* An alternative way is to first disperse in water the two components having a colloidal size and then to dry out the water.[6–8] This process induces the fusion of the polymer particles,[9] namely the latex, and therefore the incorporation of solid particles in a film or membrane like structures.

The latter strategy involves colloidal dispersions that are known to experience a sol–gel transition at a wide range of volume fractions when the particles become attracted to each other.[10] The aggregation of particles leads to the formation of fractal clusters,[11] whose kinetics depends on the volume fraction,[12–14] that may fill the entire space and form a soft colloidal gel network. This transition is mainly governed by the interaction potential between the particles that sets its kinetic type, *i.e.* diffusion limited or reaction limited. Moreover, the aggregation of colloids can be induced under shear[15] where the hydrodynamic energy input may overcome any barrier in the interaction energy between two particles.[16,17] For binary systems, the destabilization of the dispersions can be triggered by different particle charges, sizes or chemical compositions.[18]

In this work, we follow the colloidal dispersion pathway for elaborating an elastomeric composite material based on natural rubber (NR) latex and carbon black (CB). Carbon black can be dispersed into pure water but large aggregates are formed, a few tens of microns, and a sol–gel transition is observed at a relatively low volume fraction. If the carbon black dispersion is mixed with natural rubber latex now, a heterogeneous coagulum is instantaneously obtained. Once compressed between fingers, this coagulum easily turns into an elastic solid that resists tension, *i.e.* the binary mixture undergoes an irreversible transformation. These observations led us to investigate by which physical process this remarkable

---

[a] *ESPCI ParisTech, LCMD, UPMC Univ. Paris 06, UMR 7195, 10 rue Vauquelin, 75231 Paris, France. E-mail: Nicolas.Bremond@espci.fr*

[b] *Manufacture Française des Pneumatiques Michelin, 23 Place des Carmes Déchaux 63040, Clermont-Ferrand Cedex 9, France*

† Current address: Grupo de Sistemas Complejos, Universidad Complutense de Madrid, Ciudad Universitaria – 28040 Madrid, Spain.

phenomenon is governed and by which physicochemical parameters this transition is controlled. The investigation is mainly based on rheological characterizations of binary colloidal mixtures. Ultimately, a process can be designed for manufacturing homogeneous elastic composite materials. This novel process that involves an aqueous medium is not restricted to film structures since the material arises from a bulk destabilization of the colloidal mixture.

2 Results and discussion

Surfactants are commonly used for dispersing hydrophobic particles in water. Here, we use sodium dodecyl sulfate (SDS) for improving the dispersion state of CB during a sonication step and for ensuring the colloidal dispersion stability.[19] We observe that for a given CB volume fraction ϕ_{CB} there exists a critical SDS concentration above which the binary colloidal dispersion does not become an elastic coagulum while being stirred. To be more quantitative, we investigated the mechanical features of the binary colloidal mixture.[20] The mechanical response of the mixture under oscillatory shear, namely the complex shear modulus $G = G' + iG''$, is characterized as a function of the SDS concentration C_{SDS} of the mixture for a fixed NR and CB composition that is $\phi_{NR} = 0.22$ and $\phi_{CB} = 0.028$. The time evolution of the two moduli, where the time zero corresponds to the beginning of the rheological measurements, are shown in Fig. 1 for three surfactant concentrations. We first note that the elastic modulus G' is an order of magnitude higher than the viscous modulus G''. Then, while G'' is nearly constant, G' starts from a non-zero value G'_0 and increases with time until it reaches a plateau G'_m. The time evolution of G' is well described by an exponential function of the type

$$G'(t) = G'_m - (G'_m - G'_0)\exp(-t/\tau),$$

where τ is a characteristic time of this first-order kinetic like process.[21] We do not observe any evident dependence of τ on the amount of the surfactant that lies between 350 s and 800 s.

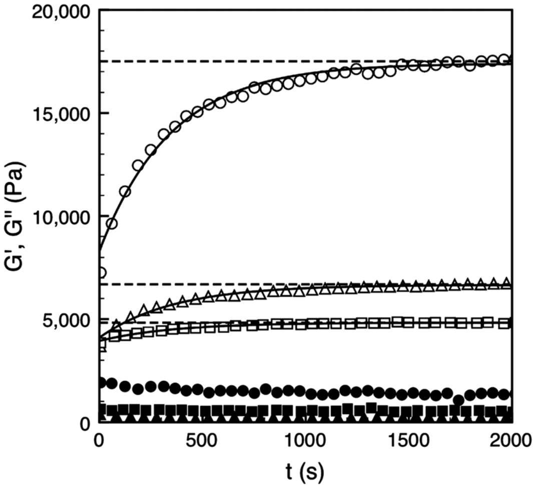

Fig. 1 Time evolution of the elastic modulus G' (empty symbols) and the viscous modulus G'' (filled symbols) of a natural rubber and carbon black mixture ($\phi_{NR} = 0.22$ and $\phi_{CB} = 0.028$) for three SDS concentrations: 16.5 mM (○, ●), 17.4 mM (△, ▲) and 17.8 mM (□, ■). The continuous lines reveal an exponential relaxation of G' towards its equilibrium value G'_m indicated by horizontal dashed lines.

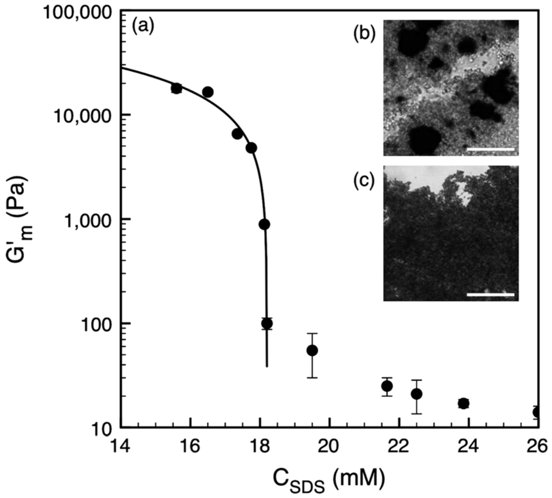

Fig. 2 (a) Plateau values G'_m reached by the elastic modulus of a natural rubber and carbon black mixture ($\phi_{NR} = 0.22$ and $\phi_{CB} = 0.028$) as a function of the SDS concentration C_{SDS} in the binary colloidal dispersions. The curve is a critical-like function reflecting a gel–elastic solid transition. Pictures taken under a microscope of the mixture with SDS concentrations equal to (b) 15.5 mM and (c) 17.5 mM. The scale bars are 50 μm.

On the other hand, the plateau value G'_m reached by the elastic modulus is a decreasing function of C_{SDS}, as reported in Fig. 2(a). The elastic modulus starts at a relatively high value, a few tens of kPa, and then dramatically decreases when the surfactant concentration approaches $C_{SDS}^{c} = 18.2$ mM. This jump is then followed by a slow decrease of G'_m towards much lower values close to a few Pa. We note that G'' follows the same trend. The first regime is well described by a critical-like function that is a signature of a fluid–solid like transition of attractive colloidal particles,[10] *i.e.* $G'_m = G'_U(C_{SDS} - C_{SDS}^{c})^{\nu_U}$ where $\nu_U \sim 0.8$. The adsorption state of the surfactant on CB particles is directly linked to the interparticle attractive energy U that is a decreasing function of C_{SDS}.[22,23] Here, since two classes of particles are coming into play, the interaction may involve either two identical particles or two different particles. As it will be discussed later on, a heteroaggregation scenario is occurring. Pictures taken with a microscope of the colloidal dispersion are also reported in Fig. 2 for a low value of C_{SDS} (Fig. 2(b)) as well as a concentration close to the critical one (Fig. 2(c)). We clearly see that the homogeneity of the mixture is improved at a higher SDS content.

Measuring the surface tension of a colloidal dispersion is a standard way to characterize the adsorption state of surfactant molecules on solid particles that is linked to the dispersion stability.[24] The surface tension γ as a function of C_{SDS} is reported in Fig. 3 for a pure solution of SDS and two volume fractions of CB equal to 0.028 and 0.056. The latter volume fraction corresponds to that of the initial CB dispersion that is then mixed with the NR latex with a dilution factor of 1/2 (see Section 3 for more details). We clearly observe a shift of the critical micellar concentration (CMC) towards higher values when the amount of particles, and thus the accessible surface area, is increased. The

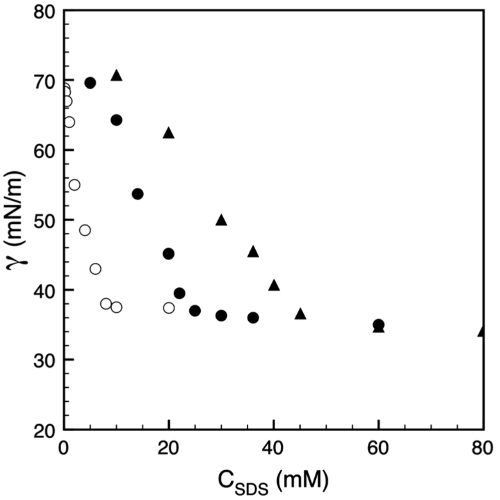

Fig. 3 Surface tension of carbon black dispersions as a function of the SDS concentration for various volume fractions of particles: (○) $\phi_{CB} = 0$, (●) $\phi_{CB} = 0.028$ and (▲) $\phi_{CB} = 0.056$.

CMC values are around 8 mM, 24 mM and 47 mM for ϕ_{CB} equal to 0, 0.028 and 0.056, respectively. Thus, for $\phi_{CB} = 0.028$, the new critical micellar concentration, which corresponds to a full coverage of the CB particles, is above the critical concentration C^c_{SDS} below which the irreversible transition takes place (Fig. 2(a)).

The particularity of the present binary colloidal system is that it undergoes a transition from a weak gel towards an irreversible elastic solid. Indeed, for SDS concentrations lower than C^c_{SDS}, the mixture turns into an elastic solid that resists tension. We mention that at the end of the experiment, when the cone of the rheometer is lifted up, a thin elastic sheet is uncovered. Then, for a larger amount of surfactants, the mixture becomes a weak gel that is reversible. Moreover, as it will be shown later, this gel can then be transformed into an irreversible elastic solid when a high shear is applied. We therefore conclude that in this regime, for $C_{SDS} > C^c_{SDS}$, there exists an energy barrier between the two types of particles to overcome in order to form an elastic solid. Otherwise, the particles may be trapped in a secondary minimum of the interaction potential that can ultimately form a weak gel.[25] Here, the surfactant molecules that adsorb on CB particles are anionic and thus confer electrostatic and steric repulsions between them. These two repulsion forces also prevent the rubber droplets to coalesce since they are naturally stabilized with phospholipid–protein complexes that are negatively charged as well.[26] Therefore, Coulombic and steric repulsions between CB and NR may lead to the existence of a secondary minimum of the interaction potential.

What happens if the natural rubber volume fraction is varied while all other component contents are kept fixed? The plateau values of the elastic modulus G'_m are reported in Fig. 4 as a function of ϕ_{NR} for $\phi_{CB} = 0.028$. In that case, the initial SDS concentration used for dispersing CB particles is just below the transition threshold and equal to 18.1 mM. We observe that for ϕ_{NR} larger than 0.2, G'_m sharply increases until it reaches a maximum value of 10^4 Pa for ϕ_{NR} around 0.29. Then, the elastic modulus of the mixture falls and vanishes for ϕ_{NR} larger than 0.44. Again, the increase of G'_m is well described by a critical-like function of the NR volume fraction, *i.e.* $G'_m = G'_\phi(\phi_{NR} - \phi^c_{NR})^{\nu_\phi}$, where $\phi^c_{NR} = 0.2$ and $\nu_\phi \approx 1.8$. The fall of G'_m exhibits a rather different critical exponent ν_ϕ close to 2.5. Even though the rise and the fall of G'_m are not symmetrical, these features reveal an irreversible transition from a weak gel, that is reversible, towards an elastic solid. Here, the volume fraction of the NR particles governs this transition and can be assimilated to the density of a jamming system.[10] We finally note that if we keep the volume fraction of NR constant and increase the amount of CB, the elastic modulus also increases but we end up with a less cohesive material. Moreover, most of the final material is reversible when water is added, a characteristic shared by the weak gel phase.

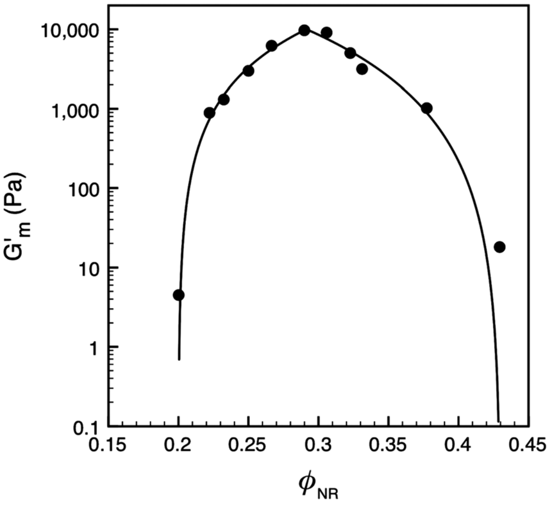

Fig. 4 Plateau values of the elastic modulus G'_m of natural rubber and carbon black mixtures as a function of the NR volume fraction for fixed CB and SDS contents ($\phi_{CB} = 0.028$ and $C_{SDS} = 18.1$ mM). The curves represent critical-like functions.

From the previous observations, we can conclude that the binary colloidal mixture undergoes a structural transition where the carbon black particles are bridging the natural rubber particles together as sketched in Fig. 5. This bridging phenomenon allows the formation of a spanning network of fractal clusters that results in the formation of an elastic solid[10] as illustrated by case b in Fig. 5. This transition is principally governed by the interparticle attractive energy between CB particles and NR droplets that is tuned by the surfactant

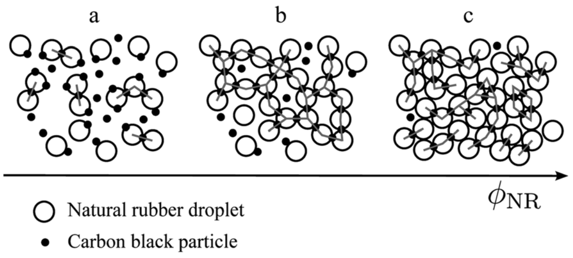

Fig. 5 Sketches of the heteroaggregation process when the volume fraction of NR is increased while keeping the amount of CB constant. The gray lines show the networks formed by NR droplets bridged together with CB particles.

concentration (Fig. 2). Even though the microscopic mechanisms involved in the interaction between NR and CB are still not well understood and deserve further investigations, the depletion force induced by surfactant micelles can be dismissed since both NR and CB dispersions are stable for a concentration of SDS up to 50 mM. Moreover, since the transition is based on a heteroaggregation process, the relative amount of both colloids matters. Indeed, as revealed by the mechanical properties shown in Fig. 4, if too much NR is added into the mixture, the transition does not occur any more. Therefore, the lack of CB particles needed to link clusters between them precludes any percolation of the system as represented by case c in Fig. 5. This behavior is also observed for specific biological interaction between colloids when the amount of linkers in the solution is tuned.[27] Finally, for a fixed volume fraction of NR, increasing the quantity of CB may result in a network made of homoaggregates of CB particles among heteroaggregates since the final material is less cohesive.

As mentioned in the Introduction, one of the intriguing observations is that the colloidal gel can turn into an elastic coagulum once sheared. This observation reminds us of the destabilization of an oil in water emulsion under shear when silica particles are introduced into the continuous phase.[28] We thus study the mixture behavior under a steady shear when the SDS concentration is above $C^{\mathrm{c}}_{\mathrm{SDS}}$, *i.e.* in the weak-gel state. The time evolution of the effective shear viscosity η is reported in Fig. 6(a) for a steady shear rate $\dot{\gamma}$ of 400 s^{-1}. The mixture composition is $\phi_{\mathrm{NR}} = 0.22$, $\phi_{\mathrm{CB}} = 0.028$ and $C_{\mathrm{SDS}} = 22.5$ mM. We observe an induction time prior to an increase of η that goes through a maximum and then decreases. It has been proposed that such rise of the viscosity results from a shear activated aggregation process,[16] an assumption recently confirmed by a theoretical analysis.[17] A characteristic time t_{c} of the heteroaggregation process can be estimated by the intersection of the two asymptotes[16] as shown in Fig. 6(a). This induction time is a decreasing function of the shear rate that tends to have an exponential decrease as reported in Fig. 6(b). This exponential behavior is a signature of a thermally activated process.[16] In that case, the hydrodynamic force between colloids, which is generated during the collision of the particles induced by the shear flow, reduces the activation energy barrier to overcome for aggregating the particles. For monodisperse colloids, the corresponding hydrodynamic energy scales as $\eta_{\mathrm{s}}\dot{\gamma}a^3$, where η_{s} is the shear viscosity of the solvent and a is the particle's radius. Finally, the induction time t_{c}, which arises from the characteristic time of the irreversible aggregation of two particles, is expected to vary according to the expression $t_{\mathrm{c}} \approx \exp(-\alpha\eta_{\mathrm{s}}\dot{\gamma}a^3/k_{\mathrm{B}}T)$, where α depends on the type of flow and the particle volume fraction.[16,17]

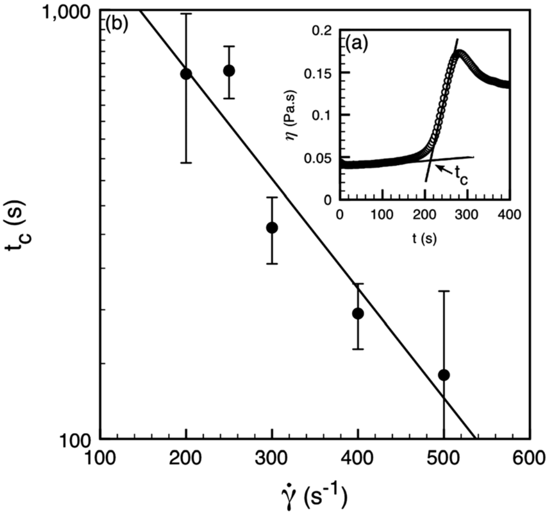

Fig. 6 (a) Time evolution of the effective shear viscosity η of a mixture having a composition $\phi_{\mathrm{NR}} = 0.22$, $\phi_{\mathrm{CB}} = 0.028$ and $C_{\mathrm{SDS}} = 22.5$ mM. The measurements are performed under a steady shear rate $\dot{\gamma}$ of 400 s^{-1}. The induction time t_{c} is defined by the intersection of the two asymptotes. (b) Induction time t_{c} as a function of the shear rate $\dot{\gamma}$ of the same mixture as in (a). The continuous line is an exponential fit revealing a thermally activated process.

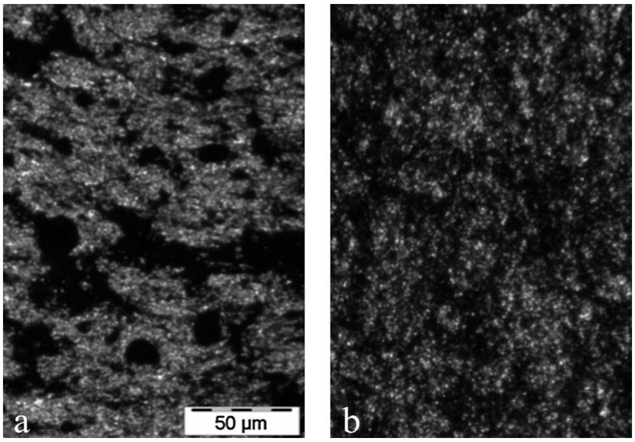

Fig. 7 Pictures observed under a microscope with reflected light of the surface of dried coagulum slices: (a) without SDS and (b) with SDS. The final volume ratio between NR and CB is 4 and $C_{\mathrm{SDS}} = 16$ mM.

The weak gel or the elastic coagulum can finally become a highly cohesive elastic solid once dried. Indeed, the evaporation of water induces the coalescence of the NR droplets[9] that naturally incorporate the mineral colloids. Pictures of the dried coagulum slices are shown in Fig. 7 for a mixture prepared without and with SDS. The pictures are obtained under microscope with reflected light where dark regions correspond to higher concentrations of CB particles. As expected, we note that the CB is more homogeneously distributed into the polymer matrix when SDS is used for dispersing the CB particles in water.

3 Materials and methods

Natural rubber is an elastomer that is principally composed of isoprene polymers. It is mainly produced by Hevea trees in a colloidal dispersion, namely latex. The NR particles floating in an aqueous medium are stabilized by a shell made of negatively charged phospholipid–protein complexes.[26] The field latex contains about 30% rubber among non-rubber solid particles and it is then concentrated by centrifugation to about 60% rubber content.[29] Finally, ammonia is added for preventing bacteria proliferation and it leads to the hydrolysis of phospholipids to fatty acid soaps. In this study, we use a NR latex (Astlett Rubber) having a density of 0.92 g cm^{-3} at a weight fraction of 0.61 that corresponds to an initial volume fraction ϕ^0_{NR} equal to 0.63. The diameter of the NR particles is around 0.8 ± 0.16 μm as measured by static light scattering (Mastersizer S, Malvern).

Carbon black is an amorphous form of carbon resulting from an incomplete combustion of fuels.[30] The CB (Cabot) grade used in the present experiments is N234 that is characterized by a density of 1.8 g cm^{-3} and a surface area of 120 m^2 g^{-1}. CB is a colloidal cluster of primary particles having a size of around 20 nm and a fractal dimension of 2.2.[31] It is dispersed in distilled water by sonication (Vibracell model 75042, power: 500 W) at 60% of the full power for 2 minutes. At a relatively low volume fraction, about 0.006, CB particles form larger aggregates until a gel phase is reached. We then use surfactants such as sodium dodecyl sulfate (SDS) for improving the dispersion state of CB during the sonication step and for ensuring the colloidal dispersion stability.[19] The final aggregate diameter is around 160 nm as measured by dynamic light scattering (Zetasizer, Malvern). These indissociable aggregates are considered as the CB particles throughout this work.

The adsorption of surfactant molecules on CB particles is thought to be driven by hydrophobic interactions and occurs on non-polar carbon surface patches.[32] Here, the adsorption state is characterized by measuring the surface tension γ of CB dispersions as reported in Fig. 3. The particles are centrifuged away and the surface tension of the supernatant is determined by the pending drop method (DSA30, Kruss).

Binary colloidal dispersions are made as follows. First, the CB particles are dispersed in water under sonication at a given volume fraction, which is 0.056 for most of the experiments reported in this article, and with an initial concentration C^0_{SDS} of SDS. Then, the same volume of NR latex at various volume fractions is added to the CB dispersion. The resultant concentration of the surfactant is thus half the initial one. The mixture is then slowly stirred by hand in a beaker with the help of a spatula. After about one minute, the mixture acquires a uniform color and becomes a gel that can be spooned off for further rheology experiments.

The rheological features of the binary colloidal mixture are characterized by using a controlled-shear rate rheometer (Rheometrics RFSII) with a cone/plane geometry having a diameter of 50 mm and a minimal gap size of 45 μm. The temperature is maintained at 23 °C during all the measurements. We note that depending on the SDS concentration, the weak gel can easily turn into an elastic solid. Therefore, special care has to be taken when the sample is loaded into the rheometer. The rheological properties of the mixture are either probed in a low strain oscillating regime, the strain γ being 0.2%, and at a relatively low frequency of 1 Hz, or under a steady shear with a shear rate ranging from 200 s^{-1} to 500 s^{-1}.

4 Conclusion

In this article, we proposed and characterized a novel way to form an elastomeric composite material. The process is based on a bulk destabilization of a binary colloidal mixture composed of hydrophobic solid particles and polymer droplets. This route gives rise to a process that is not restricted to polymer film formation. The two types of hydrophobic particles, natural rubber latex and carbon black, are either naturally stabilized or dispersed in water with the help of surfactants. The system undergoes a heteroaggregation phenomenon whose characteristics are mainly controlled by the amount of surfactants. Indeed, the adsorption of surfactant molecules onto the carbon black surface tunes the interaction between the two types of particles and thus the homogeneity of the dispersion before its destabilization. For more stable situations, the energy barrier that inhibits the bridging effect can be overcome by applying a shear. To the best of our knowledge, such a destabilization where hydrophobic solid particles bridge polymer droplets has never been reported so far. Because of potential technological applications, like tire manufacturing, this kind of binary colloidal dispersions deserve further investigations. One of the major fundamental questions to be addressed is to understand the origin of the high reactivity between CB and NR particles and thus the underlying interactions that are involved in this remarkable irreversible heteroaggregation. We believe that understanding the microscopic mechanisms that rule this transition will open the way to make composite elastomeric materials from synthetic latexes and with other hydrophobic fillers.

Acknowledgements

We acknowledge the PPMD group from ESPCI ParisTech, and especially Guylaine Ducouret, for giving us access to their rheology facilities.

References

1 J. N. Coleman, U. Khan, W. J. Blau and Y. K. Gun'ko, *Carbon*, 2006, **44**, 1624–1652.
2 S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen and R. S. Ruoff, *Nature*, 2006, **442**, 282–286.
3 J. L. Leblanc, *Prog. Polym. Sci.*, 2002, **27**, 627–687.
4 L. Bokobza and O. Rapoport, *J. Appl. Polym. Sci.*, 2002, **85**, 2301–2316.
5 G. Heinrich, M. Kluppel and T. A. Vilgis, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 195–203.
6 N. Grossiord, J. Loos, O. Regev and C. E. Koning, *Chem. Mater.*, 2006, **18**, 1089–1099.
7 J. C. Grunlan, A. R. Mehrabi, M. V. Bannon and J. L. Bahr, *Adv. Mater.*, 2004, **16**, 150–153.
8 J. Oberdisse, *Soft Matter*, 2006, **2**, 29–36.
9 M. Joanicot, K. Wong and B. Cabane, *Macromolecules*, 1996, **29**, 4976–4984.
10 V. Trappe, V. Prasad, L. Cipelletti, P. N. Segre and D. A. Weitz, *Nature*, 2001, **411**, 772–775.
11 D. A. Weitz and M. Oliveria, *Phys. Rev. Lett.*, 1984, **52**, 1433.
12 J. Bibette, T. G. Mason, H. Gang and D. A. Weitz, *Phys. Rev. Lett.*, 1992, **69**, 981.
13 M. Carpineti and M. Giglio, *Phys. Rev. Lett.*, 1992, **68**, 3327.
14 P. Poulin, J. Bibette and D. A. Weitz, *Eur. Phys. J. B*, 1999, **7**, 277–281.
15 W. B. Russel, D. Saville and W. R. Schowalter, *Colloidal Dispersions*, Cambridge University Press, Cambridge, 2001.
16 J. Guery, E. Bertrand, C. Rouzeau, P. Levitz, D. A. Weitz and J. Bibette, *Phys. Rev. Lett.*, 2006, **96**, 198301.
17 A. Zaccone, H. Wu, D. Gentili and M. Morbidelli, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2009, **80**, 051404.
18 J. M. Lopez-Lopez, A. Schmitt, A. Moncho-Jorda and R. Hidalgo-Alvarez, *Soft Matter*, 2006, **2**, 1025–1042.
19 M. S. Strano, V. C. Moore, M. K. Miller, M. J. Allen, E. H. Haroz, C. Kittrell, R. H. Hauge and R. E. Smalley, *J. Nanosci. Nanotechnol.*, 2003, **3**, 81–86.
20 T. F. Tadros, *Adv. Colloid Interface Sci.*, 1996, **68**, 97–200.
21 C. J. Rueb and C. F. Zukoski, *J. Rheol.*, 1997, **41**, 197–218.
22 C. G. de Kruif, *Langmuir*, 1992, **8**, 2932–2937.
23 V. Trappe and D. A. Weitz, *Phys. Rev. Lett.*, 2000, **85**, 449–452.

24 A. Zaccone, H. Wu, M. Lattuada and M. Morbidelli, *J. Phys. Chem. B*, 2008, **112**, 1976–1986.
25 R. C. Kramb and C. F. Zukoski, *Langmuir*, 2008, **24**, 7565–7572.
26 K. Cornish, D. F. Wood and J. J. Windle, *Planta*, 1999, **210**, 85–96.
27 A. L. Hiddessen, S. D. Rodgers, D. A. Weitz and D. A. Hammer, *Langmuir*, 2000, **16**, 9744–9753.
28 J. Legrand, M. Chamerois, F. Placin, J. E. Poirier, J. Bibette and F. Leal-Calderon, *Langmuir*, 2005, **21**, 64–70.
29 M. M. Rippel, L. T. Lee, C. A. P. Leite and F. Galembeck, *J. Colloid Interface Sci.*, 2003, **268**, 330–340.
30 J. Donnet, R. Bansal and M. Wang, *Carbon Black: Science and Technology*, Dekker, 1993.
31 W. Xu, T. W. Zerda, H. Yang and M. Gerspacher, *Carbon*, 1996, **34**, 165–171.
32 X. Chen, M. Farber, Y. M. Gao, I. Kulaots, E. M. Suuberg and R. H. Hurt, *Carbon*, 2003, **41**, 1489–1500.