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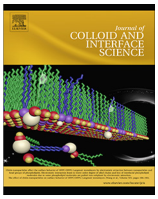

Regular Article

Colloidal polymer composites: Are nano-fillers always better for improving mechanical properties?

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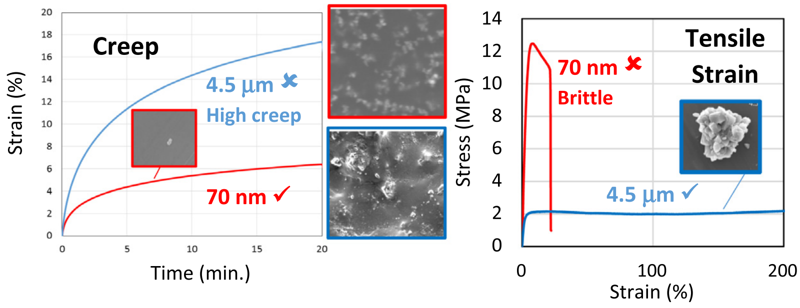
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Colloidal polymer composites, in which polymer particles are blended with a filler, are widely used in applications including pharmaceuticals, crop protection, inks, and protective coatings. It is generally found that the presence of hard particulate fillers will increase the elastic modulus of a polymer colloid composite. However, the influence of the size of the filler particle on the large-strain deformation and fracture and on the viscoelastic characteristics, including creep, is not well explored. We hypothesize that the size ratio of the filler to the colloidal polymer will play a critical role in determining the properties of the composite.
Experiments: Colloidal composites were prepared by blending soft polymer colloids (as a binder) with calcium carbonate fillers having four different sizes, spanning from 70 nm to 4.5 µm. There is no bonding between the filler and matrix in the composites. The large-strain deformation, linear viscoelasticity, and creep were determined for each filler size for increasing the filler volume fractions (ϕ_{CC}). Weibull statistics were used to analyze the distributions of strains at failure.
Findings: We find that the inclusion of nano-fillers leads to brittle fracture at a lower ϕ_{CC} than when µm-size fillers are used. The data interpretation is supported by Weibull analysis. However, for a given ϕ_{CC}, the storage modulus is higher in the rubbery regime, and the creep resistance is higher when nanoparticles are used. Using scanning electron microscopy to support our arguments, we show that the properties of colloidal composites are correlated with their microstructure, which can be altered through control of the filler:polymer particle size ratio. Hard nanoparticles pack efficiently around larger particles to provide reinforcement (manifested as a higher storage modulus and greater creep resistance), but they also introduce weak points that lead to brittleness.

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1. Introduction

Composites of inorganic fillers in a polymer matrix can be processed from a polymer in a good solvent, from a melted thermoplastic, or from a thermosetting resin. An alternative method of using colloidal polymer particles allows easy mixing with inorganic fillers at nanometer length scales when dispersed in the same liquid, typically water [1]. Under the right conditions, the polymer particles deform and coalesce to make a continuous polymer matrix upon drying. Colloidal composite coatings find numerous applications in inks [2], crop protection [3], pharmaceuticals [4], cosmetics [5], and paints [6].

The colloidal approach has been used widely to distribute inorganic nano-fillers (i.e. having at least one dimension less than 100 nm) in polymer nanocomposites. In an early example, Grunlan et al. [7,8] produced nanocomposite coatings with a 'segregated network' of carbon nanotubes (CNTs) evenly dispersed at the boundaries between colloidal polymer particles. There are numerous other examples of segregated networks of CNTs being used to improve the mechanical and adhesive properties of nanocomposites [9–13]. Other research has investigated effects of silica nanoparticles [14] and inorganic fillers (TiO_2, $CaCO_3$, and kaolinite) with varying aspect ratios [15] on the elastic modulus of colloidal composites. There have been fewer studies of the large-strain deformation, creep and fracture of colloidal nanocomposites. Notably however, the failure under tensile strain of colloidal nanocomposites made from hard/soft blends has been studied in experiments [16].

In *non-colloidal* polymer composites, such as composites formed from epoxy resins [19], thermoplastics [17], and solvent-based polymers [18], significant progress has been made in understanding the effects that filler size [19], shape [20], interfacial adhesion [10], and particle loading (volume fraction of filler particles) have on the Young's modulus, strength and toughness. For these *non-colloidal* polymer composites, the Young's modulus has been demonstrated to increase with increasing inorganic particle loading [21–24]. In this class of composite, the Young's modulus is largely unaffected by filler particle size [17,25–30], unless it is decreased to a critical size of *ca.* 30 nm [31–33]. Since the Young's modulus is measured at low strain, it has been consistently observed to be largely unaffected by the particle/matrix interfacial adhesion [34–37].

Likewise, the strength of a composite, measured as the maximum stress achievable without failure under uniaxial tensile testing, is affected by addition of filler particles. For *non-colloidal* composites with strong adhesion between the filler and the matrix, decreasing the mean filler particle size results in increased strength [38–41]. When the filler particles are tightly bound to the matrix, they can support an applied load, and therefore an increase in the filler loading results in a stronger composite. Regarding the fracture properties of *colloidal* composites, there have been a few experimental studies of the effect of the volume fraction of hard filler particles on the tensile strength, with data described by empirical equations [42]. However, the experiments and equations neglect to consider the effects of the filler: binder particle size ratio, α, which we hypothesize will be particularly critical.

In relation to colloidal nanocomposites used for coatings, it is relevant to introduce the concept of the critical pigment volume concentration (CPVC) [6]. When hard pigment (or filler) particles are added at increasing concentrations to a coating matrix, there will be a critical volume fraction above which there is a sharp increase in opacity resulting from the development of air voids because of a lack of sufficient binder. At concentrations above the CPVC, coatings gain opacity, and there is often a simultaneous onset of cracking and void formation [6,43].

An empirical equation has been proposed in the literature [43] to relate the number ratio of filler: binder particles at CPVC to their size ratio, α. In experiments, del Rio and Rudin [43] varied α from 0.25 to 3 and found an increase in the CPVC (measured via gloss measurements) from approximately 30 vol% to more than 50 vol %. However, they did not study the corresponding mechanical properties. In a complementary study [6], α was increased from 1 to 3 by changing the size of the hard pigment particles, which led to an increased porosity and decreased gloss. However, the corresponding mechanical properties were not reported; thus there is a need for this current research.

Previous research on colloidal composites has explored the effects of nanoparticles of various compositions, for example, silica [14,44], titania [15], and calcium carbonate [45,46], to name but a few, on mechanical properties, but have not compared the effects of fillers with dimensions both greater and less than 1 μm (or a wide range of size ratios) in the same studies. Systematic studies of filler size over a wide range in colloidal composites are lacking. Furthermore, although the elastic modulus is often studied in colloidal nanocomposite, the fracture and creep properties are often neglected. This work aims to address these gaps in current understanding.

We specifically consider a materials system in which the filler (precipitated calcium carbonate) is not bonded to the continuous phase that is formed from a colloidal acrylic copolymer. In such a system, "nano" effects [47] arising from reduced mobility of macromolecules confined in an interphase between the filler and matrix are not expected. We investigate the polymer in both the rubbery and glassy regimes through variation of the experimental temperature and the addition of a volatile plasticizer to lower the T_g. We determine the critical impact of the size of the filler (whether less than 100 nm or greater than 4 μm) on the large-strain deformation and fracture properties in combination with the viscoelasticity and creep. We determine those properties for which nanofillers provide the greatest enhancement and those for which they are detrimental.

2. Materials and methods

2.1. Latex synthesis

Latices were prepared by emulsion polymerization of styrene (St), butyl acrylate (BA) and acrylic acid (AA) at POLYMAT, The University of the Basque Country UPV/EHU, (Donostia-San Sebastián, Spain). 0.8% sodium lauryl sulphate (SLS) was added as a surfactant. A 1 wt% solution of sodium 4-[2-(4-morpholino)benzoyl-2-dimethylamino]butyl benzene sulfonate (MBS) and potassium sulphate (KPS) in a 1:1 M ratio was used as an initiator. A monomer ratio of 4.95:4.95:1 of St:BA:AA made a poly(St-BA-AA) copolymer in a latex with a solids content of 40 wt%. The particle size, according to dynamic light scattering (Malvern Zetasizer Nano Series, Malvern, UK), is 175 nm.

2.2. Calcium carbonate suspensions

Samples of precipitated calcium carbonate powders, with four different mean sizes (70 nm, 0.7 μm, 3 μm, and 4.5 μm), were obtained from Minerals Technologies (New York, NY). The larger particles consist of aggregates of smaller calcium carbonate crystals. The density of the particles is reported by the manufacturer to be 2.71 g cm^{-3}.

Suspensions of calcium carbonate in water were made by adding 5 g poly(acrylic acid) as a dispersant to 45 g of water to make a 10% w/w solution. Calcium carbonate powder was added slowly to