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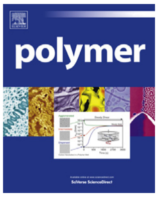

Superhard transparent hybrid nanocomposites for high fidelity UV-nanoimprint lithography

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ABSTRACT

Transparent hyperbranched acrylate nanocomposites were produced using different combinations of silica nanoparticles and silicon-based sol–gel precursors. The nanocomposites were processed using a dual-cure UV polymerization and condensation scheme. The viscosity of hybrid suspensions was found to be one to two orders of magnitude lower than that of particulate composites with the same equivalent silica fraction. The Vickers microhardness of the polymer was 112 MPa. It was equal to 190 MPa and 148 MPa for the hybrid composites and particulate composites with 20 vol% SiO_2, respectively, and it was equal to 287 MPa for the hybrid material with 30 vol% SiO_2. Light-trapping textures in the form of random sub-micron pyramidal features were replicated in the hybrid composites from a nickel template using UV-nanoimprint lithography. After optimization of the dual-cure process sequence, a very high replication fidelity was obtained for all investigated compositions, leading to a haze above 99% over the visible light spectrum and a very effective light scattering performance in a broad angular exposure.

1. Introduction

Hybrid materials based on a combination of organic and inorganic precursors and produced using sol–gel processes have emerged in the last two decades and stimulated numerous research efforts as recently reviewed by Drisko and Sanchez [1]. Polymer nanocomposites based on preformed nanoparticles mixed with the polymer also enjoy great attention, with a focus on enhanced thermo-mechanical performance [2]. For both sol–gel and particulate composite materials the combination of organic and inorganic phases and their interactions give rise to outstanding mechanical properties such as toughness [3] and microhardness [4], diffusion barrier properties, flexibility and optical transparency [5,6]. Precursors are also often low cost and are compatible with cost-effective processing methods, including photopolymerization and roll-to-roll (R2R) processing [7,8]. These attributes make such nanocomposite materials good candidates for the encapsulation of flexible devices as OLEDs [5] or thin film silicon solar cells [9].

The numerous benefits of particulate nanocomposites depend on a good dispersion of the nanoparticles. Avoiding particle agglomeration is challenging and often requires tailored particle surface modification. Another problem is related to the very large specific interfacial area. In this case, even small amounts of nanoparticles may drastically increase the viscosity of the composite, so the liquid-like polymer is transformed into a solid-like composite. As an example, it was found that the addition of 5 vol% of 12 nm diameter silica nanoparticles to an acrylate monomer led to gelation of the suspension, and that at 20 vol% of nanoparticles the viscosity increased by more than five orders of magnitude [10]. Such processing problems can be overcome by using solvents. An alternative is, in fact, the sol–gel route, whereby the liquid inorganic precursors enable a low viscosity of the hybrid solution to be maintained, thus avoiding the problematic liquid-to-solid transition of the particulate suspensions. This process moreover enables a very homogeneous dispersion of the reactants at the molecular level, hence of the inorganic phase within the polymerized matrix [8,11–14]. The resulting sol–gel composites are thus very versatile since the contributions of the organic and inorganic phases and their interactions can be carefully tailored. This enables accurate control of a broad range of properties, particularly for optical and protective coating applications [11,15]. However, the mechanical properties of the sol–gel composites are lower than those obtained with particulate composites, since the inorganic component acting as a network former does not contribute to the material properties based on its physical state properties [8,16] to the same degree as in the case of preformed nanoparticles.

Focus of the present work is on the development of light-trapping textures based on hybrid silica-hyperbranched polymer

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(HBP) nanocomposites. HBPs are globular molecules with high reactivity and Newtonian viscosity [17], low polymerization shrinkage [18] and good compatibility with inorganic components [19,20]. Particulate and sol–gel nanocomposites based on a UV-curable HBP with improved thermomechanical stability and hardness compared to the unreinforced HBP have been reported in recent works [9,18]. Moreover, these nanocomposite materials enabled sub-micron sized structures to be replicated with a very high fidelity using UV nanoimprint lithography (UVNIL) owing to their low shrinkage. The low pressure, low temperature and short time needed to create nanocomposite replicas using UVNIL are all favorable for implementation in printing industries [21]. However, the liquid-to-solid transition of particulate nanocomposites at low particle fraction, or the long condensation time of sol–gel nanocomposites might invalidate the UVNIL process. The objective of the present work was thus to explore an alternative route, with the aim of achieving a balanced viscosity between the particulate and sol–gel cases, while minimizing the process cycle time and maximizing the mechanical properties of the final material. The approach was to combine nanoparticles, HBP and sol–gel precursors to form multi-scale hybrid nanocomposites (e.g. Refs. [8,16]). The combination of controlled rheology and high hardness should be advantageous for the fast production of hard coats, and of functional coatings with tailored surface textures.

2. Experimental section

2.1. Materials and processing

The HBP was a polyester acrylate oligomer with a functionality of 16, a density of 1.13 g/cm^3 and a glass transition temperature in cured state equal to 165 °C (CN2302, Sartomer). The photo-initiator was 2,4,6Trimethylbenzoyldiphenyl phosphine oxide (Esacure TPO, Lamberti). The nanoparticles were methacrylated amorphous fumed SiO_2 in the form of nanopowder aggregates with a primary particle size of 12 nm and a specific surface area of about 150 m^2/g (Aerosil R7200, Evonik). The organometal precursor was tetraethylorthosilicate (TEOS, Sigma–Aldrich). Methacryloxy(propyl)trimethoxysilane (MEMO, Sigma–Aldrich) was used as a coupling agent.

Three different nanocomposites were developed, namely particulate composites, sol–gel composites and hybrid composites; their composition is detailed in Table 1. In all cases the photoinitiator was first dissolved in the HBP at 75 °C at a concentration of 6 wt% and stirred for 15 min. Following references to HBP will always refer to the mixture of HBP with 6 wt% photoinitiator.

Particulate composites were prepared by solvent-assisted mixing of the HBP with the methacrylated silica particles. The particles were first dispersed in isopropanol (ratio 1:3 by weight) and sonicated to disagglomerate the aggregates (400 W, Digital Sonifier, Branson). A selected amount of SiO_2 suspension was then added to the HBP and the mixture was stirred for 1 h. The corresponding particle volume fraction was calculated assuming a density of 2.2 g/cm^3 for fused silica. The solvent was then evaporated at 60 °C under vacuum until no more weight variation of the suspension was detected. Particulate composites with up to 30 vol% of SiO_2 were prepared.

Sol–gel composites were produced in three steps, by mixing the HBP with MEMO first, then adding TEOS, and finally 1 M HCl in water (Sigma–Aldrich). Acidic conditions ($pH \leq 2$ in the present case) combined with the presence of the coupling agent ensured the formation of a fine silica network rather than aggregates [18]. After each step the mixture was stirred at room temperature until homogenization was visually observed. After addition of HCl the mixture was further stirred for 30 min. Composites with up to 20 vol% of silica were prepared. The volume fraction of SiO_2 in the cured composite was calculated assuming a density of 2.0 g/cm^3 for the sol–gel silica. A corresponding amount of TEOS was calculated assuming 100% conversion of the precursor into SiO_2. The amount of coupling agent was calculated to give a concentration of 10% methacrylic groups within acrylic groups. Conversion of the silanol groups into SiO_2 was also assumed to be 100%. The amount of H_2O was calculated to give a molar ratio of H_2O to ethyl groups equal to 1:2.

Hybrid composites were prepared by combining the direct mixing and sol–gel processes, using both silica particles and a liquid silica precursor. A suspension of the methacrylated silica nanoparticles in the HBP was prepared first as described above for the particulate composites. MEMO and TEOS were subsequently mixed with the suspension and the mixture was stirred until homogenization was visually observed. 1 M HCl in H_2O was eventually added and the hybrid suspension was further stirred for 30 min. Composites with up to 30 vol% of silica, including up to 20 vol% of silica resulting from the condensation of TEOS were prepared. The volume fraction of silica in the suspensions and in the cured composites was the sum of the particles fraction and the sol–gel silica fraction. In the case of the suspensions, the volume fraction of silica should be considered as an equivalent fraction to enable comparison with the particulate suspensions.

It was found that the hybrid suspensions containing an increasing concentration of TEOS were less stable and gelled faster when stored at ambient temperature for several days. It was in fact shown that for solutions having a pH lower than the isoelectric pH, namely 2.2 for silica, the gel time decreased with the acidity of the solution [12]. This explains the differences of stability that we observed, since the acidity of the solution increased with the amount of TEOS (the HCl:TEOS ratio was kept constant). Sol-gel

Table 1

Composition of particulate, sol–gel and hybrid composites and dual-cure process timing for sol–gel and hybrid composites. Dashes indicate that no coatings were produced.

Composite abbreviation	SiO_2 nanoparticles [wt%]	SiO_2 nanoparticles [vol%]	TEOS [wt%]	MEMO [wt%]	Silica from TEOS [vol%]	Condensation time before UV-polymerization [min]	Total condensation time [h]
5A	9.3	5	0	0	0	–	–
5T	0	0	13.8	8.5	5	240	4
10A	17.8	10	0	0	0	–	–
10T	0	0	24.8	6.9	10	240	4
5A_5T	9.6	5	12.5	7.7	5	–	–
3A_10T	6	3	23.3	6.5	10	2, 6, 15, 30, 45	4
5A_10T	9.8	5	22.3	6.3	10	–	–
20A	32.7	20	0	0	0	–	–
20T	0	0	39.6	4.8	20	240	4
10A_10T	18.7	10	20.2	5.6	10	30, 45	4
5A_20T	10.1	5	35.2	4.4	20	6, 8[a], 10[a]	1, 4
30A	45.5	30	0	0	0	–	–
10A_20T	19.3	10	31.6	3.9	20	6	4

[a] Replication fidelity not very high.