Enhancing the Mechanical Properties of Matrix-Free Poly(Methyl Acrylate)-Grafted Montmorillonite Nanosheets by Introducing Star Polymers and Hydrogen Bonding Moieties

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Matrix-free nanocomposite films of poly(methyl acrylate) (PMA) and montmorillonite (MMT) nanosheets that imitate the microscopic structure of nacre are developed and their mechanical properties are studied in detail via tensile testing. The exfoliated MMT nanosheets are grafted with PMA via a grafting-through radical addition–fragmentation chain transfer polymerization in presence of a surface-anchored ionic monomer. The mechanical properties are precisely tailored a) via the variation of the degree of polymerization of the surface-grafted polymer, illustrating the impact of chain entanglement and the MMT content on the performance of the material, and b) via cross-linking of the surface-grafted polymer, either by partial change of the polymer topology from linear to star-shape or by the introduction of hydrogen-bonding units within the polymer. These experiments demonstrate the strong influence of the chain mobility of the surface-grafted polymer on the mechanical properties of the nanocomposite material.

1. Introduction

Conventional polymer–nanocomposites consist of nanosized inorganic fillers and a polymeric matrix and with increasing filler content an improved mechanical performance is expected.[1–3] When the matrix polymer content is reduced to zero, “matrix-free” composites, consisting only of particles and surface-bound organic molecules, can be obtained.[4–6] Tchoul et al. prepared titanium dioxide-polystyrene matrix-free composites by combination of phosphonate coupling and “click”-chemistry resulting in composites with up to 80 wt.-% of inorganic contents.[7] Choi et al. synthesized both polystyrene- and poly(methyl methacrylate)-grafted silica nanoparticles and produced a material consisting only of particles and surface-tethered polymer chains. They could observe a dependency of the materials Young’s modulus, fracture toughness, and hardness on the degree of polymerization (DP) of the grafted polymer.[8] Crucial for the successful preparation of such materials is the presence of interactions between different particles through entanglement of polymer chains bound to different particles. This is given if the chains are long enough to entangle with each other or if the chains are cross-linked.[6] Additionally, research strives for achieving an order of the particles as it is hoped to produce materials with, for example, superior optical properties.[6,8]

One naturally occurring “matrix-free” material with exceptional mechanical properties is nacre, which consists of 95 vol.-% of aragonite platelets and 5 vol.-% of organic biopolymer.[9] They form a composite with a “brick-and-mortar”-like structure, which exhibits exceptional mechanical properties. The Young’s modulus is known to be up to 135 GPa accompanied by a fracture toughness of up to 1.8 MJ m$^{-2}$. These properties can be assigned to the unique structure of this special material.[9,10] A biomimetic approach to produce a similar synthetic material is the use of layered nanoparticles, substituting the aragonite, and synthetic organic molecules to replace the natural biopolymer. Different nanoparticles, such as graphene oxides,[11,12] Al$_2$O$_3$ platelets,[13] or nanoclays,[4,10,14,15] have been used so far.

In this publication, we report the successful preparation of a nacre-like material using montmorillonite (MMT) nanosheets and for the first time PMA to form self-standing films and explore new strategies to tailor their mechanical properties by modifying the polymer functionalization of the platelets. Using the soft and ductile PMA allows for the formation of nanocomposites that show an exceptionally high modulus and tensile strength without being brittle. The mechanical properties of the novel material are further enhanced by cross-linking of the surface-grafted polymer, which is either achieved via radical addition–fragmentation chain transfer (RAFT) star-polymerization upon the platelet surface or via introducing hydrogen-bonding moieties to the surface-grafted polymer.
2. Results and Discussion

MMT nanosheets were grafted with PMA by first functionalizing the surface with an ionic monomer via an ion-exchange reaction and subsequently forming surface-linked polymer via a grafting-through RAFT polymerization using the RAFT agent 1) (see Figure 1).[16–18] The modification of the particles with linear PMA of varying DP and their detailed characterization has been reported by our group recently.[17] Additionally, particles were grafted with a mixture of star and linear polymer in a single-step RAFT polymerization using different ratios of RAFT agents (1) and (2) (see Figure 1). Finally, nanosheets grafted with polymer that are physically cross-linked via hydrogen bonds were prepared by adding 2-carboxyethyl acrylate (CEA) as comonomer in small quantities. As discussed in our preceding publication, we thoroughly characterized the polymer-coated nanoparticles using thermogravimetric analysis (TGA), size-exclusion chromatography (SEC), attenuated total reflection Fourier transform infrared spectroscopy, near field scanning optical microscopy (s-SNOM), and small-angle X-ray scattering in order to confirm the successful surface modification with PMA.[17]

For the successful formation of thin, self-standing films, the PMA-grafted MMT nanosheets were dispersed in propylene glycol monomethyl ether acetate (PGMEA) (4 wt.% MMT in PGMEA) and transferred into a teflon mold. The molds were covered loosely with a lid and the solvent was evaporated slowly at room temperature for 48 h followed by further drying at 100 °C in vacuo resulting in films of approximately 0.8 mm thickness. Due to the high aspect ratio of the MMT sheets and the slow evaporation speed, it can be assumed that the nanosheets mostly align parallel to the mold surface forming a “brick-and-mortar”-like structure.[10,20–22] The obtained films were characterized with scanning electron microscopy (SEM) to provide optical impressions of this structure (see Figure 2). As evident from the micrograph, cross-section and surface show a different topography due to the proposed orientation of the nanosheets, with the surface appearing smoother in comparison to the rougher cross-section area.

2.1. Films from MMT Grafted with Linear Polymer

In a first approach, MMT was modified with linear PMA of different DP in order to determine its influence on the mechanical properties of the resulting films (Table 1, for SEC curves of the grafted polymer and dispersity values, which were between 1.1 and 1.4, see Supporting Information). From sample L-I, no self-standing film could be produced, because the films were too brittle. This gives rise to the assumption that a minimal grafted polymer DP is required to form continuous films. In order to form stable films, the polymer chains on the particles apparently need to interact with chains grafted onto other particles, presumably via chain entanglements that provide a connecting force between particles. For polymers, the entanglement molecular weight describes the limit above which chains are able to entangle with each other, while below that limit the chains are described as rods. For PMA, the entanglement molecular weight is known to be approximately 1.1·10^4 g mol⁻¹ or 128 monomer units.[23] As the molecular weight of L-I is below that limit, no entanglement between chains is expected which is confirmed by the fact that no continuous film could be produced.

From samples, L-II to L-VII films were successfully prepared and analyzed via tensile testing. Representative stress–strain-curves are shown in Figure 3 and obtained values for Young’s modulus E, strain-at-break ε, tensile strength σ, and toughness...
Table 1. Degree of polymerization DP, Young’s modulus E, strain-at-break \( \varepsilon \), tensile strength \( \sigma \), and toughness \( U_T \) of self-standing films made from MMT nanosheets grafted with linear PMA. Values are averages of eight to twelve measurements and errors are standard deviations. DP is calculated as DP = \( \frac{M_r}{M_{monomer}} \).

| Sample | DP | \( E/10^2 \) [N mm\(^{-2}\)] | \( \varepsilon \) [%] | \( \sigma \) [M Pa] | \( U_T/10^4 \) [J m\(^{-3}\)] |
|--------|----|----------------|-------|-------|--------------|
| L-I    | 46 | -              | -     | 18.0 ± 2.1 | 0.4 ± 0.1    |
| L-II   | 139 | 22.1 ± 2.3    | 3 ± 1 | 12.5 ± 1.3 | 26 ± 4       |
| L-III  | 209 | 21.5 ± 1.2    | 3 ± 1 | 22.8 ± 1.1 | 20.7 ± 1.5   |
| L-IV   | 256 | 18.5 ± 1.5    | 9 ± 1 | 22.8 ± 1.1 | 14.6 ± 1.3   |
| L-V    | 325 | 12.5 ± 1.3    | 26 ± 4| 20.7 ± 1.5 | 14.8 ± 1.5   |
| L-VI   | 372 | 6.69 ± 0.17   | 50 ± 10| 16.8 ± 1.1 | 9.6 ± 0.9    |
| L-VII  | 453 | 5.56 ± 0.32   | 68 ± 14| 14.8 ± 1.5 | 7.6 ± 2.1    |
| L-VIII | 500 | 2.76 ± 0.12   | 154 ± 26| 12.5 ± 1.1 | 13.7 ± 3.2   |

\( U_T \) are given in Table 1. All samples show exceptionally high values for modulus and tensile strength, being up to two orders of magnitude higher than values obtained for the pure polymer.[17,24] The Young’s modulus and the tensile strength of the films decrease with increasing grafted DP. At the same time both the toughness and the strain-at-break increase. Each film consists of the same amount of MMT, so when the DP of the grafted polymer is increased, the overall polymer content of the material inerently decreases—assuming identical grafting densities—and the MMT fraction in the film is accordingly reduced. The influence of the softer PMA increases, consequently resulting in a decrease in Young’s modulus. At the same time, as the polymer chains get longer, the interaction between them increases. When the film is exerted to an external uniaxial tensile force, the interacting chains withstand this force providing mechanical stability to the film. With increasing external force, the grafted chains disentangle which can be observed as plastic deformation. The higher the DP, the more plastic deformation prior to breaking is observed. In contrast to unfilled thermoplastics above their glass transition, as for example PMA, where the chains can flow freely when an external stress is applied, all samples show a distinct breaking point due to the fact, that all chains are anchored to the surface of nanosheets and can therefore not flow unendingly. In all cases, the highest stress that could be applied to the sample was the stress-at-break. As a combination of this and the increasing strain-at-break, the toughness of the material increases with increasing grafted chain length or polymer content.

2.2. Films from MMT Grafted with Cross-Linking RAFT Star Polymer

The introduction of cross-links is a well-known strategy to tune the mechanical properties of a polymer. One strategy for the introduction of cross-links is a change in the topology of the polymer by using RAFT star polymers. It has been shown that star polymers have a higher effective bridge connection in copolymers.[25,26] It can therefore be concluded that the interaction between different chains is enhanced, which makes them suitable to further tune the mechanical properties of the MMT-PMA films.

The chosen star RAFT agent (Figure 1) is a three-arm star RAFT agent.[19] As it is designed as a so-called R-star RAFT agent, it can be used in combination with the linear RAFT agent (Figure 1) during the grafting-through polymerization resulting in a combination of linear and star-shaped polymer at the MMT surface. During the RAFT polymerization, radicals have the same probability to add to a trithiocarbonate group of either a star or a linear macro-RAFT agent.[25] Consequently, each arm of the star polymer and the linear polymer are expected to have the same DP. As both polymers are chemically identical but only differ in their topology, the star cores can be understood as cross-links between linear PMA. Cross-linking of linear polymer enhances the restoring forces within the network under external stress as the movement of chains is hindered and they are held in place.[27,28] We already applied the strategy of mixing star polymers to materials via the RAFT process already earlier for the enhancement of mechanical properties of biomimetic spider-silk analogons.[24,25] For the present system, it is expected, that the cross-linking of the surface-bound polymer reduces their chain mobility and results in an enhanced mechanical performance of the composite films. In consequence, a higher Young’s modulus and a reduced strain at break are expected. Via TGA it was ensured, that all samples that are compared here have the same overall polymer content of 56.3 ± 1.2 wt%.

Figure 4 shows representative stress-strain-curves of films made from MMT grafted with linear and star polymer. Table 2 gives the corresponding values for the average Young’s modulus, tensile stress, strain at break, and toughness. Tensile testing clearly shows the impact of the change in polymer topology of the surface-bound polymer. Initially, when the star RAFT content is increased from 30 to 60 mol%, the Young’s modulus of the samples is increased. This can be attributed to the increasing cross-link density within the polymer shell that enhances the material’s ability to withstand external stress. This is also clearly visible in the results of the strain at break that is significantly reduced throughout this experiment because the added cross-links prevent plastic deformation of the samples. The tensile strength of samples S-I to S-IV is rather constant.
In consequence, the toughness decreases, as would be expected for a more rigid material. When the star RAFT content is increased above 80 mol%, the Young’s modulus and tensile strength decrease again. A possible explanation for this observation is that with increasing star RAFT content the number of trithiocarbonate groups is increased as well, which results in a decrease of the average DP—according to the basic rules of reversible deactivation radical polymerization—as the overall polymer content is kept constant. As discussed before, a consequence of this is that the chain’s ability to entangle with each other is reduced. This gives rise to the conclusion, that a medium star RAFT content is most favorable for enhancing the mechanical performance of these nanocomposites.

2.3. Films from MMT Grafted with Polymer that Undergoes Hydrogen Bonding

The introduction of hydrogen bonding moieties to polymers by using a small fraction of comonomers carrying H-bonding sites is a strategy that has already been shown to result in excellent mechanical properties of polymers, as shown by us and others.[24,29,30] It is known that these kinds of polymers can absorb high amounts of energy when subjected to external stresses due to breaking and reforming of H-bonds.[24] The outstanding advantage of this approach lies in the reversibility of this process: Once the external loading is ending, the flexible polymer chains relax and new H-bonds can be reformed allowing for the same or even higher mechanical resilience.[24] CEA was chosen as comonomer to provide H-bonding moieties. Poly-CEA is known to have a low glass transition temperature of $T_g \approx 22 ^\circ C$ and its successful RAFT polymerization has already been reported.[16] The fact that the glass transition temperature is relatively close to the glass transition temperature of PMA ($\approx 10 ^\circ C$) allows for the conclusion that all enhancing effects can be attributed to the introduction of cross-links and not to the introduction of more rigid parts to the polymer backbone. The CEA content was determined via NMR spectroscopy. Using a combination of gravimetry and the knowledge of the CEA content allowed to ensure that all samples had a very similar DP of 411 $\pm$ 8. Representative stress-strain-curves are shown in Figure 5 and values for modulus, tensile strength, strain-at-break, and toughness are given in Table 3. The impact of the H-bonding moieties is clearly visible: The Young’s modulus was increased by a factor of four, while the strain at break was decreased by a factor of ten and the tensile strength was doubled. The toughness decreases in consequence. The introduction of H-bonds, therefore, opens up the possibility to keep a high polymer content, which may for example be associated with better resistance against water, while maintaining extraordinary mechanical properties.

3. Conclusion

Within this paper, we presented the successful preparation of mechanically stable, thin MMT-PMA films with precisely tailorable mechanical properties. The strategy of combining a soft and ductile polymer with the rigid MMT layered silicate—inspired by natural nacre—results in the formation of a polymer matrix-free material that perfectly combines the ductility and plastic properties of a soft polymer with the high...
Table 3. Young’s modulus $E$, strain-at-break $ε$, tensile strength $σ$, and toughness $U_t$ of films made from MMT nanosheets grafted with different ratios of star and linear polymer. Values are averages of eight to twelve measurements and errors are given as standard deviation.

| Sample | CEA content [mol%] | $E/10^7$ [N mm$^{-2}$] | $ε$ [%] | $σ$ [M Pa] | $U_t/10^4$ [J m$^{-2}$] |
|--------|---------------------|------------------------|---------|-----------|-----------------------|
| HB-I   | 0                   | 6.7 ± 0.2              | 5 ± 10  | 1 ± 1     | 5.7 ± 1.5             |
| HB-II  | 3                   | 15.7 ± 1.1             | 1 ± 2   | 1 ± 1     | 1.3 ± 0.9             |
| HB-III | 7                   | 23.4 ± 5.4             | 5 ± 1   | 2 ± 1     | 0.7 ± 0.3             |

4. Experimental Section

Materials: 2-(Dodecylthiocarbonothioylthio)propionic was purchased from Sigma Aldrich and used without further purification. Azobis(isobutyronitril) (AIBN, ≥ 99%, Fluka) was recrystallized from methanol and stored at −18 °C. Methyl acrylate (MA, Sigma Aldrich) and CEA (Sigma Aldrich) were purified by passing through a column of basic alumina (Sigma Aldrich) to remove the inhibitor. Sodium MMT was filtered with teflon filters (Th. Geyer GmbH, Renningen, Germany) of 0.45 mm pore size. All given SEC results are number average molecular weights obtained by evaluation of the RI signal.

Scanning Electron Microscopy (SEM): Scanning electron microscopy was performed using a Type FEI Nova NanoSEM 650 in ultra high vacuum using an operating voltage of 3.0 kV. All samples were coated with gold prior to the measurement to ensure conductivity of the sample.

Thermogravimetric Analysis: TGA was performed with a Netzsch TG 209 F3 Tarsus over a temperature range from room temperature to 1000 °C with a heating rate of 10 K min$^{-1}$. All samples were dissolved in THF (c = 3 g L$^{-1}$) containing Toluene as an internal standard (c = 10–8 mol L$^{-1}$). Prior to injection, all samples were filtered with teflon filters (Th. Geyer GmbH, Renningen, Germany) of 0.45 mm pore size. All given SEC results are number average molecular weights obtained by evaluation of the RI signal.

Supporting Information

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

Acknowledgements

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.
Keywords
hydrogen bonding, mechanical properties, montmorillonite, nanocomposites, RAFT polymerization, star polymers

Received: January 26, 2021
Revised: February 15, 2021
Published online: March 9, 2021

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