

Sepiolite fibers improve the mechanical and shape-memory properties of polyurethane

Hongxiang Chen and Guihui Yu

Sepiolite fibers are incorporated in a simple and practical method to achieve increased tensile strength characteristics and shape fixity ratios of polyurethane composites.

Shape-memory polymers are ‘smart’ materials that can change, upon subjection to some kind of external stimulus (e.g., heating), from a deformed state to their original shape. One example—shape-memory polyurethane (SMPU)—has shown great potential for applications in several fields, including medicine,^{1–3} electronics,^{4,5} packaging,⁶ and textiles.^{7,8} SMPU consists of alternating hard and soft segments, and this material exhibits combined molecular design flexibility, large deformability, and good processability. The tensile modulus and shape fixity ratio of SMPU, however, still need to be improved.

The addition of nanofillers into a matrix has emerged as a useful way to improve the mechanical properties of polymers. Indeed, it has previously been shown that the shape-memory properties of SMPU can also be improved in this way, for example, with the use of carbon nanotubes,⁹ graphene,^{10–12} chitin,¹³ and cellulose nanocrystals¹⁴ as the nanofillers. However, it was not possible with any of these previous filler materials to simultaneously improve both the tensile modulus and shape fixity ratio of SMPU.

In our work, we have demonstrated that sepiolite (a fibrous hydrated magnesium silicate mineral) can be used to improve the mechanical properties and thermal stability of polyurethane.^{15,16} These improvements are possible because of the strong interactions that occur between the sepiolite and polyurethane. The influence of the sepiolite fibers on the crystallization of the SMPU soft segments and its shape-memory properties, however, have yet to be investigated. In our most recent work,¹⁷ we have therefore prepared SMPU composites that are modified with sepiolite, to study how the incorporation of the sepiolite affects the polyurethane structure. We prepared the SMPU composites by reacting poly(ϵ -caprolactone) and 1,4-butanediol with 4,4'-diphenylmethane diisocyanate, and including a different sepiolite weight fraction in each sample (up to 5% sepiolite). We thus

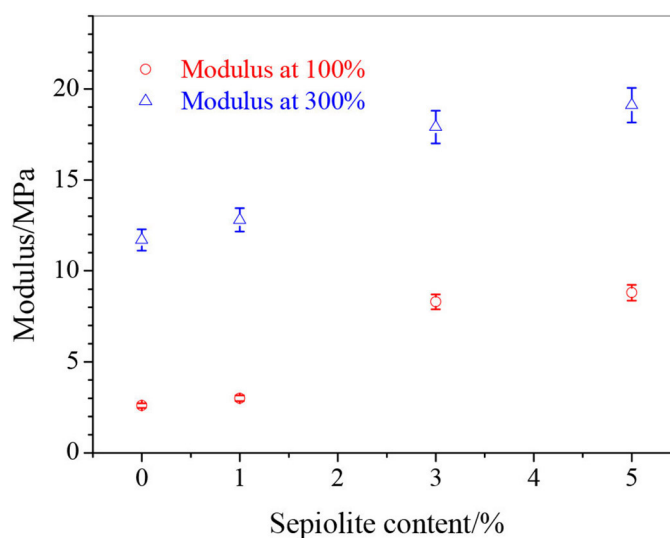


Figure 1. Tensile modulus values of pristine polyurethane (with 0% sepiolite content) and three shape-memory polyurethane (SMPU) nanocomposite samples (containing 1, 3, and 5% sepiolite). Results are given for 100 and 300% elongation conditions.

refer to each composite in the form SMPU-X, where X is the weight fraction of sepiolite with respect to the polyurethane. We then conducted a series of tests (i.e., dynamic mechanical analysis, differential scanning calorimetry, x-ray diffraction, and polarized optical microscopy) to characterize the structure and properties of our composites.

The tensile stress values of our SMPU composites at 100 and 300% (i.e., at 100 and 300% elongation) are expressed in Figure 1. These results indicate that the tensile moduli of the composites, at both 100 and 300% elongation, are higher than those of a pristine SMPU composite (containing no sepiolite). In addition, we find that the tensile modulus increases with increasing sepiolite content and that there is an especially large jump between the SMPU-1 and SMPU-3 samples. We

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are able to achieve uniform dispersion of the sepiolite fibers within the SMPU matrix because of their strong interaction with polyurethane. The interfacial interaction (i.e., between sepiolite and SMPU) of the composites therefore increases with increasing sepiolite content, which means sepiolite plays an important role in the transferral of stress during the tensile process. Our results thus indicate that the addition of sepiolite can be beneficial to improving the modulus (tensile strength) of polyurethane elastomers.

In our work we also used a camera to record the shape recovery of the different SMPU specimens. In these tests, we first heated strips of the neat SMPU (i.e., SMPU-0), SMPU-1, SMPU-3, and SMPU-5 samples to 60°C. We held the samples isothermally at this temperature for three minutes and bent them into the shapes of the letters W, U, S, and T. In the next step, we cooled the samples to -10°C for five minutes. We also maintained the samples at this temperature for a further three minutes after releasing the stress. Finally, we heated the deformed specimens again to 60°C and kept them at this temperature for six minutes so that we could recover their initial shapes. We repeated this cycle three times to check the reproducibility of the shape memory effect. As illustrated in Figure 2, the shapes of the composites were fixed well at the low temperature, and they were able to recover the initial shapes after the subsequent temperature elevation.

To study the influence of the sepiolite on the shape-memory properties, we determined the shape fixity ratio (R_f) for each of the samples. This ratio is a measure of the reversible melt-crystal transition of the soft segment phase in shape memory polymers and can be calculated as:

$$R_f(N) = \frac{\epsilon_u(N)}{\epsilon_m(N)} \times 100\% \quad (1)$$

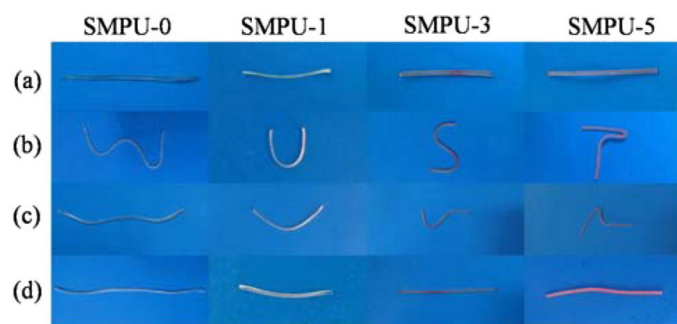


Figure 2. Photographs of SMPU-0, SMPU-1, SMPU-3, and SMPU-5 samples (containing 0, 1, 3, and 5% sepiolite, respectively) at various stages of the shape-recovery testing. The images show the samples (a) in their initial shape, (b) in their temporary shape (after heating to 60°C and bending into various shapes), (c) after reheating at 60°C to recover the initial shapes, and (d) in their final shape.

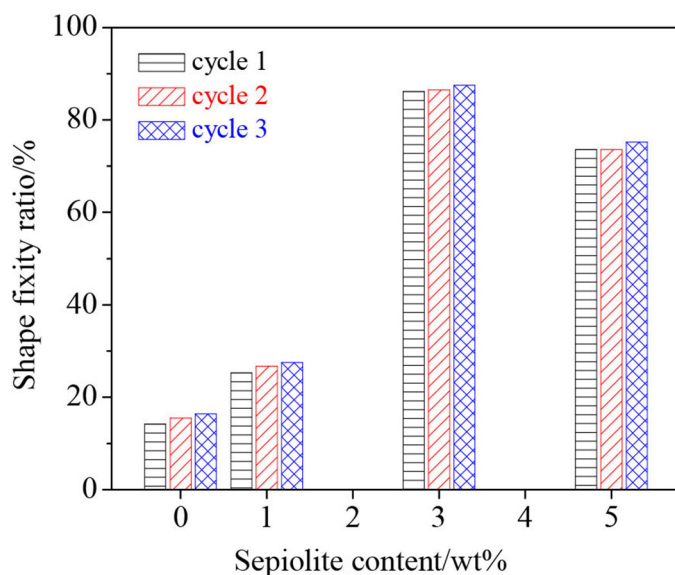


Figure 3. The shape fixity ratio of the pristine polyurethane and the SMPU composite samples, as a function of sepiolite content, after the three shaping cycles.

where ϵ_m is the maximum strain under the loading conditions, ϵ_u is the fixed strain (stabilized at -10°C) under unloading conditions, and N is the number of shaping cycles. Our results (see Figure 3) show that the R_f values for the composites are higher than that of the SMPU-0 sample. Furthermore, we observe that R_f first increases, and then decreases, with increasing sepiolite content after the first shaping cycle. We also find that R_f of the pristine SMPU and the composites increases slightly after each cycle. These trends can be explained by the fact that the inclusion of sepiolite gives rise to a nucleation effect in the soft segment phase of the SMPU. The crystallinity of the soft segments is therefore larger in the composites than in the SMPU-0 sample, and it seems to reach a maximum with a sepiolite content of 3%.

In summary, we have experimentally demonstrated a practical method for improving the tensile modulus and shape fixity ratio of shape-memory polyurethane samples. By including sepiolite fibers into the SMPU structure, we can substantially enhance both the mechanical and shape-memory properties of the SMPU composites. In this way, the utility of SMPU can be broadened for a number of applications. In the next phases of our work we plan to investigate how precise changes in the temperature conditions will affect our samples. We will also study the potential use of our composites for a biomimetic device and other medical applications.

Author Information

Hongxiang Chen and Guihui Yu

Wuhan University of Science and Technology
Wuhan, China

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