Plastics Research Online
SOCIETY OF PLASTICS ENGINEERS
10.2417/spepro.006965

Creep-recovery behavior of novel polyurethane/carbon nanotube composites

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Dynamic mechanical analysis and three well-known models were used to investigate the mechanical properties of samples synthesized from recycled poly-ethylene terephthalate.

Poly-ethylene terephthalate (PET) bottles (patented in 1973[1]) account for 83–84% of the total current demand for PET resin.[2] The large amount of waste PET—in the form of disposed plastic bottles—therefore presents a substantial environmental problem.[3] As PET is naturally resistant to degradation, recycling of PET waste is thought to be an effective way to reduce the environmental impact of this plastic.[4] For instance, recycling PET bottles leads to the conservation of fossil fuels, thereby reducing energy consumption and greenhouse effects.[2] Although such low-cost physical recycling of PET is widely adopted in large-scale applications, the recovered PET tends to have reduced clarity and poorer mechanical properties.

As an alternative to physical recycling of PET, chemical recycling can be used to produce a variety of value-added products, including polyurethanes (PUs).[5–7] Indeed, PUs are an important class of copolymer in the engineering sector because they exhibit many attractive properties (e.g., adjustable mechanical strength, good chemical resistance, and potential shape-memory) and recycled PET could therefore have a large market.[8] To obtain the desirable PU properties, however, it is necessary to compound the PU with an inorganic filler. For example, carbon nanotubes (CNTs) have previously been used to improve the stiffness, strength, toughness, and conductivity of PU.[9,10] Furthermore, the relaxation behavior—e.g., the creep-recovery characteristics—of PU/CNT composites have been investigated.[11] Creep is an important material property that determines dimensional stability and it is essential to realizing long-term durability and reliability of polymers.[12] The creep behavior of PU/CNT nanocomposites has therefore been the focus of several previous studies.[13,14] To date, however, the creep-recovery characteristics of CNT composites made with PET-recycled PU have not been examined.

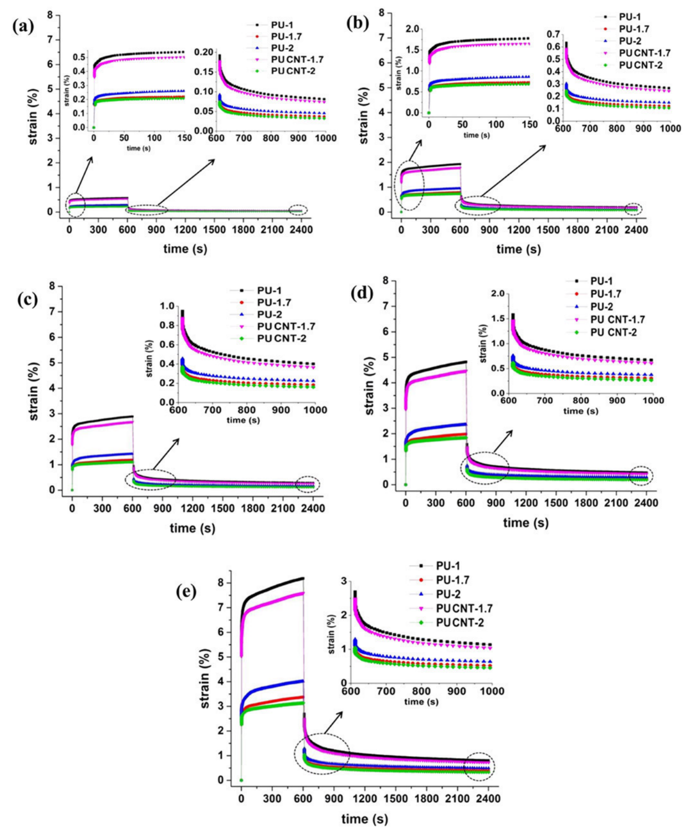

Figure 1. *Experimentally measured creep and creep-recovery strain, as a function of time, for the polyurethane (PU) and PU/multiwalled carbon nanotube (CNT) nanocomposites at 30°C. Results are shown for stress levels of (a) 0.5MPa, (b) 1MPa, (c) 1.5MPa, (d) 2MPa, and (e) 2.5MPa. Sample details are given in Table 1.*

In this work,[15] our aim was therefore to produce a new set of PU composites from recycled PET and to study the creep-recovery characteristics of the samples. To that end, we synthesized polyester diol via glycolysis of the recycled PET waste. We used this diol to prepare our

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Table 1. *The composition, physical state, and stress–strain properties of the PU and PU/CNT samples. NCO/OH: Isocyanate/hydroxyl ratio.*

Sample	NCO/OH (molar ratio)	CNT (wt%)	Physical state	Young's modulus (MPa)	Offset yield stress (MPa)
PU-1	1	–	Thermoplastic	30.3	4
PU-1.7	1.7	–	Thermoset	60	10.7
PU-2	2	–	Thermoset	51	8.5
PUCNT-1	1	0.5	Powder	–	–
PUCNT-1.7	1.7	0.5	Thermoplastic	37	3.7
PUCNT-2	2	0.5	Thermoplastic	81.8	7.4

PU and multiwalled CNT (MWCNT) nanocomposites (see Table 1). In addition, we performed a dynamic mechanical analysis (DMA) to measure the creep-recovery properties of the samples at seven different stress levels (0.5, 1, 1.5, 2, 2.5, 5, and 8MPa). The full details of our synthesis method for the PU nanocomposites, as well as for our DMA measurements, have previously been provided.[7, 16]

The creep-recovery results we obtained (between 0.5 and 2.5MPa) for our PU and PU/MWCNT nanocomposites are shown as a function of time in Figure 1. We observed the lowest creep and recovery strains for the PUCNT-2 sample, followed by PU-1.7, PU-2, PUCNT-1.7, and then PU-1. This trend, however, does not follow the Young's modulus results we obtained (see Table 1). We attribute the high creep-strain of the PU-1 sample to its thermoplastic nature and thus its higher capacity for slippage and viscous flow. Moreover, we believe that the lower creep-strain of PU-1.7 compared with PU-2 was caused by the higher crosslinking degree of PU-1.7.

Rather than polymeric, our PUCNT-1 sample had a powder form because of the steric hindrance effect of the MWCNT nanoparticles and the low number of diisocyanate functional groups (see Table 1) in this particular composite. Specifically, the steric hindrance effect of the MWCNTs caused a reduction in the reactions between the isocyanate and hydroxyl (OH) functional groups. This effect also gave rise to the increased creep-strain of the PUCNT-1.7 sample. In contrast, the reinforcing effect of the MWCNTs strengthened the polymers and thus reduced the creep-strain of the PUCNT-2 sample. These effects originate from the inherently high modulus of the MWCNTs and from the good interactions between the OH groups and urethane groups on the MWCNT surfaces. The results of our measurements at 5 and 8MPa were similar to the data we obtained in the 0.5–2.5MPa range. We found, however, that the creep and recovery strains for PUCNT-2 at 5MPa were higher than those of PU-1.7. We attribute this result to the proximity of 5MPa to the 7.4MPa offset yield stress for PUCNT-2 (see Table 1).

In our study, we also fitted our experimental results with a number of well-known models (i.e., that are commonly used to model creep or recovery experimental data). First, we used the power-law model[17] (a simple and common constitutive model) to examine the creep-strain–time dependency of our data. From this model we obtained several parameters, including the amplitude of the transient creep-strain (A) and the time exponent (n) of the dependency. We found that there was good agreement between the model results and the experimental data, and specifically, that the higher creep-strain samples exhibited higher values for A and lower values for n.[18] We also used the Burgers model[19] (a four-element model) to evaluate the creep behavior of our samples. We observed an inverse relationship between the creep-strain and the four Burgers parameters (i.e., the elastic strain, viscoelastic strain, and two viscoplastic strain parts) and, again, a good agreement between the model and experimental datasets. Lastly, we applied the Weibull distribution model[20] to our recovery measurements and found a good agreement with our empirical data. The results also revealed that the increased crosslink density of PU-2 and PU-1.7 (i.e., compared with PU-1) caused a decrease in the viscoelastic strain recovery (ϵ_{VI}) of the samples. The addition of MWCNTs to PU-1.7 increased the ϵ_{VI}, whereas the incorporation of MWCNTs into PU-2 had the opposite effect (i.e., evidence of the opposing steric hindrance effect of MWCNT particles).

In summary, we have synthesized novel PU nanocomposites from recycled PET waste and MWCNTs. We found that the reinforcing and steric hindrance effects of MWCNTs and the crosslinking degree of PUs are important parameters that govern the creep-recovery behavior of the samples. Our future work will be focused on other applications of these samples, and on the synthesis of nanocomposites from these PUs and alternative nanoparticles (e.g., clay, graphene, and core-shell nanoparticles).

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