

Resistance to time-dependent deformation of nanoparticle/polymer composites

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Dimensional stability and structural reliability are major concerns for thermoplastics due to their nature of high mobility of polymer chains. Here the authors report the creep experiments on polypropylene filled with 1 vol % TiO₂ nanoparticles with diameter of 21 or 300 nm at different load levels and temperatures, which show that the dimensional stability of the nanocomposites is significantly improved, especially by loading small sized nanoparticles. The creep strain and creep rate of nanoparticle-filled polypropylene are reduced by 46% and 80%, respectively, compared to those of the neat matrix. Additionally, creep lifetime is extended by 330% due to the addition of small nanoparticles. © 2007 American Institute of Physics. [DOI: [10.1063/1.2753494](https://doi.org/10.1063/1.2753494)]

Polymer materials are widely used in many fields due to their great physical and mechanical properties,^{1,2} such as lightweight, dielectric, optical transparency, acceptable toughness, etc. Polypropylene (PP) has a low density, an intermediate level of Young's modulus, toughness, and flexibility and is of great economy, which allows it to be used as a replacement for engineering plastics, ranging from living goods to automotive components to electrics, for example, dielectric thin film within certain high performance pulse and low loss radio frequency capacitors. However, time-dependent deformation is considered a main deficiency of thermoplastics in the long-term duration of practical applications, resulting in dimensional mismatch and final failure of their function. It was reported,³ for example, that a trip beaker lever is required to work at 120 °C to carry a maximum stress of 30 MPa for 10 000 h. The maximum deflection in that time must not exceed 0.1 mm. The applicable selection is to use >20% glass fiber reinforced polyamide, giving rise to large weight penalty of material and infeasibility in micro-electrics nevertheless. Consequently, it is necessary to extend new substitute materials.

With the rapid development of nanotechnologies and nanomaterials since the 1990s, studies on polymer-based nanocomposites^{4,5} have been extensively carried out to find promising alternatives of traditional composites, though mainly focused on general mechanical and physical properties and filler dispersion.⁴ Although Taneike *et al.*⁶ reported that nanocarbonitride dispersions contributed significantly to creep lifetime prolongation and creep rate reduction in steel, there are still few literatures concerning creep resistance of polymer nanocomposites.⁷⁻¹¹ Consequently, there remains a need to explore and elaborately observe the time-dependent performance of polymer nanocomposites for material design and potential engineering applications, where, for ex-

ample, the creep resistance has to be considered as a requirement.

We now report a direct observation of creep behavior of PP reinforced with different sizes of TiO₂ nanoparticles and characterized in terms of creep deformation, creep rate, and lifetime to failure. PP matrix (Moplen HP501H) is obtained from Basell Company. The as-received TiO₂ nanoparticles with diameters of 21 nm (Aeroxide P25, Degussa GmbH, Germany) and 300 nm (Kronos 2310, Kronos Titan GmbH, Germany) are applied as reinforcements without further treatment. The volume content is 1% (4.3 wt %). To obtain good dispersion of fillers, a two-step extrusion procedure was adopted. In the first step, a higher concentration of nanoparticles was compounded with the as-received matrix using a Bersdoff twin-screw extruder. In the second extrusion process, the first-step compounds were put into the feeder as fillers and the final composite granules were produced. In order to precisely control the filler content, commercial K-Tron weight-controlled feeders were applied during compounding. The composite granulates were finally manufactured by using an Arburg all-rounder injection molding machine as the dog-boned tensile specimens (160 × 10 × 4 mm³, according to the standard of ISO 527). Characterization by transmission electron microscopy (Fig. 1) of the 21-TiO₂/PP composite reveals a fairly good dispersion of nanoparticles, which may act as huge amount of immobilized sites and thus retard or block the motion of neighboring polymer chains while the material suffers from external load.

The creep measurement is performed based on ASTM 2990-01 using a creep rupture test machine (Coesfeld GmbH, model 2002). Ten specimens can be measured for the same run in an environmental chamber. For the elevated temperature measurement, the specimens in the chamber are preheated to the desired temperature for 24 h before loading in order to get a steady and uniform thermal distribution. A gauge length of 30 mm is marked on each specimen, and the displacement between the marks is monitored by a video camera, which is equipped with a program-controlled step

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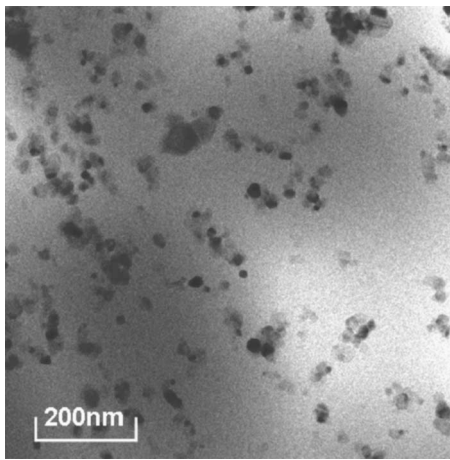


FIG. 1. TEM image of 21-TiO₂/PP showing fairly good dispersion of nanoparticles in the matrix.

motor and connected with a computer imaging analysis system during the whole period of creep testing. The pure PP, 21-TiO₂/PP (or 21/PP), and 300-TiO₂/PP (or 300/PP) specimens are tested at four stress levels (8, 11, 14, and 20 MPa) and two temperature conditions (23 and 50 °C).

Figure 2 shows some representative curves of creep strain and corresponding creep rate versus time at different temperatures and stress levels. The arrow indicates that the specimens did not fail within the observation time range. It is clearly seen that the time-dependent nondeformability of 21-TiO₂/PP is significantly enhanced with reduced creep strain and creep rate and even with extended creep lifetime at high stress level, while the enhancement of 300-TiO₂/PP is slight compared to that of neat matrix.

In order to study the time-dependent deformation in detail, we compare the creep data in Fig. 2 and find that complete creep curves are obtained under high stress levels consisting of a primary creep region, where creep rate decreases while creep strain increases obviously with time, and the tertiary creep region, where both creep rate and creep strain increase with time after reaching a minimum value, and an accelerating creep process occurs finally with failure or advanced necking of material. In the initiative creep stage below 0.1 h, the creep rate is nearly the same for all specimens under the same condition. The composites thereafter display

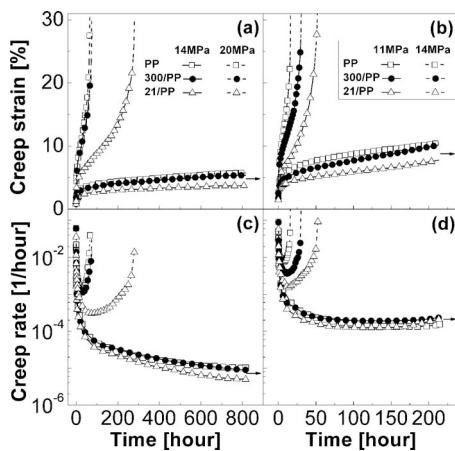


FIG. 2. Representative creep curves under different conditions. Creep deformation and corresponding creep rate vs time at [(a) and (c)] 23 °C and [(b) and (d)] 50 °C, respectively.

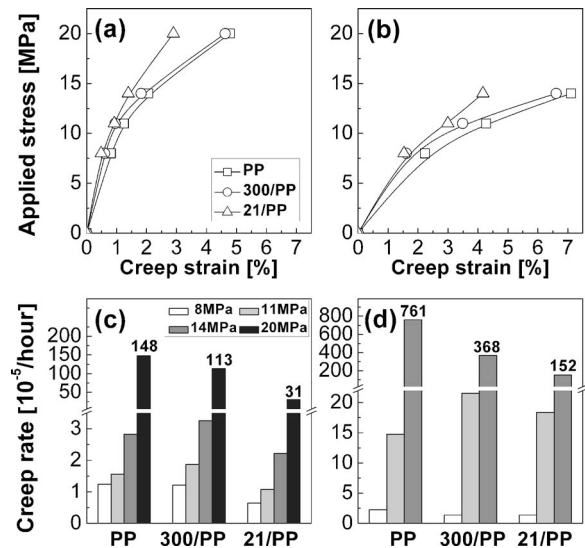


FIG. 3. Detailed deformation parameters of the specimens under all testing conditions. 1 h isochronous stress-strain relationship at (a) 23 °C and (b) 50 °C. Steady or minimum creep rate at (c) 23 °C and (d) 50 °C.

advanced decrease in creep rate with time [Figs. 2(c) and 2(d)]. Additionally, the onset of tertiary creep is retarded up to longer times by the presence of nanoparticles. This retardation leads to the longer duration of primary and secondary creep regions, which gives rise to lower minimum creep rate and longer time to failure [Figs. 2(c) and 2(d)]. Specifically, at room temperature the creep lifetimes of 300-TiO₂/PP and 21-TiO₂/PP are extended by about 17% and 320%, and their minimum creep rates are reduced by 23% and 80%, respectively, with respect to that of virgin PP under 20 MPa, as shown in Figs. 2(a) and 2(c). The reinforcing efficiency of nanoparticles is confirmed at elevated temperature. The creep lifetimes of 300-TiO₂/PP and 21-TiO₂/PP are additionally increased by 87% and 220%, and their minimum creep rates are reduced by 52% and 80%, respectively, compared to that of pure matrix under 14 MPa, as presented in Figs. 2(b) and 2(d). However, under moderate or lower stress levels, the materials endure a long-term creep process without failure even after 800 h loading [Fig. 2(c)]. Only small nanoparticle-filled PP shows a clear reduction in both creep strain and creep rate. To quantify the time-dependent deformation of the materials, the 1 h isochronous stress-strain relationship is presented in Fig. 3 at 23 and 50 °C as well as the minimum creep rate of the materials with a tertiary creep stage and the 200 h creep rate of the materials without a tertiary creep stage in the observed time scale. It is seen that at both room and elevated temperatures, 21-TiO₂/PP deforms with smaller strain amplitude by nearly 60% and lower deformation rate than PP under each stress level, which indicates that the load bearing capability is very much improved by the addition of 21 nm particles. It is noteworthy to point out that large nanoparticles show a reinforcing effect only under high loading levels, as shown in Figs. 3(c) and 3(d), with a clear reduction in creep rate. In addition, a nonlinear relationship between creep strain and applied stress implies that the materials have a nonlinear viscoelasticity under the observed stress range. The increased linearity in 21-TiO₂/PP demonstrates that the viscous flow and mobility of the polymer chains are greatly restricted by the presence of small nanoparticles. The tensile properties of the materials have been performed as well. Young's modulus, tensile

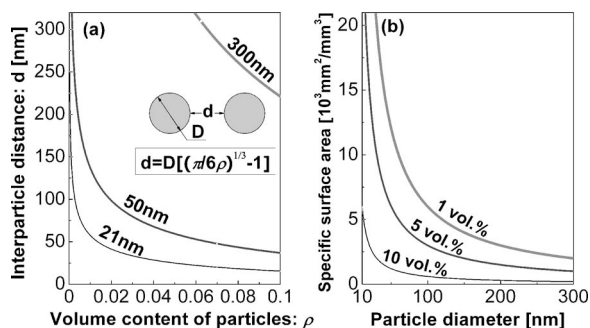


FIG. 4. Parameters of nanoparticle-filled composite based on the assumption of uniform dispersion. Interparticle distance (a) and specific surface area of fillers (b) as a function of volume content and diameter of fillers.

strength, and ductility of the composites are not changed obviously. The glass transition temperature T_g of the pure and nanoparticle-filled systems is measured using a dynamic mechanical thermoanalyzer. The obtained T_g of the filled PP ($\sim 11.6^\circ\text{C}$) was very close to that of neat PP (12.8°C), showing that the addition of nanoparticles has no significant effect on the cure properties of PP.

There are two possible mechanisms that contribute to the resultant enhancement of creep resistance: (1) a large amount of nanoparticles acting as restriction sites to retard or hinder the mobility of amorphous chains and (2) huge interfacial area and good interfacial bonding between nanoparticles and polymer matrix that benefits (1). As calculated in Ref. 9, based on the assumption of uniform dispersion, the specific particle number (defined here as the amount of particles at certain concentration in a unit volume composite) is $10^{12}/\text{mm}^3$ for 21-TiO₂/PP, which is larger than 10^9 for 300-TiO₂/PP by several orders of magnitude. Although the aggregations are difficult to avoid, the huge number of individually dispersed particles (Fig. 1) could form a network,¹² which cooperate with the matrix via interphase (to be discussed in the next paragraph), bridging segments and junctions to bear load, and improve the immobility of polymer chains.⁹ In addition, interparticle distance between two neighboring particles in 21-TiO₂/PP (60 nm) is accordingly significantly closer than that in 300-TiO₂/PP (800 nm), as shown in Fig. 4(a). Consequently, a denser and stiffer particle network in 21-TiO₂/PP greatly restricts the mobility of amorphous segments under each observed stress level (e.g., these representative dimensions including particle diameter and interparticle distance are comparable to the radius of gyration of polymer chains,^{13,14} and thus such kind of local chain motion is highly restricted); however, a looser and more compliant particle network in 300-TiO₂/PP shows that there is little resistance to the motion of polymer chains under low stress levels, while showing capability to decrease the creep rate only at higher loading level, as demonstrated in Figs. 3(c) and 3(d).

Huge specific surface area of nanofillers (defined here as the total surface area of nanoparticles at certain concentration in a unit volume composite) results in large specific interfacial region between fillers and matrix. Interfacial area is considered the most important characteristic of nanocomposites⁴ as well as of traditional composites¹⁵ since it determines the

degree of interaction between filler and matrix in terms of interfacial bonding. Additionally, a special interfacial region, namely, interphase, around the interface has been identified in a large range of 2–50 nm, where the physical and chemical properties of the matrix are gradually changed, including crystallinity, cure degree, and mobility of polymer chains.⁴ Comparatively, a specific interfacial area in 21-TiO₂/PP is larger than that in 300-TiO₂/PP by 15-folds [see Fig. 4(b)], and therefore a similar trend of interphase in the nanocomposites makes small particles much more capable to restrict and retard the mobility of amorphous segments. In this way, external load is effectively transferred to small nanoparticles, giving rise to the resulting enhancement in creep deformation.

This study has demonstrated that the service lifetime and creep resistance of the nanoparticle polymer composites are greatly improved in contrast with the neat matrix material. A very low content of 1 vol% nanoparticles contributes to these improvements with a huge number of fillers and specific interfacial area. In addition, these materials are manufactured using an industrial processing method, which could therefore strongly and economically improve grades of dimensionally stable polymer nanocomposites for large scale engineering applications.

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