

Creep response of a LDPE-based nanocomposite

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ABSTRACT: Polymer nanocomposites and their behavior have been widely investigated by several paths, including mechanical, rheological, and permeability tests, finding that several parameters (such as the polymer matrix, the nanofiller, their amounts, the presence of compatibilizers, processing parameters, etc.) can influence the main properties. However, less information is available regarding the creep response of polymer nanocomposites; in particular, few or no data are reported about the combined effect of different loads and different temperatures. In this article, the creep behavior of a low density polyethylene/organomodified clay nanocomposite has been investigated. The characterization of viscoelastic response has taken into account both the effects of applied load and temperature, which are often considered separately. Dynamic–mechanical and structural analysis was also performed in order to get a deeper understanding of the involved phenomena. The nanocomposite showed lower creep deformations (up to ~20%) and the relative differences with the neat polymer matrix were found to be increasing upon increasing the applied load (up to ~24%) and the temperature (up to ~38%). © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44180.

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INTRODUCTION

Polymer-based nanocomposites are a relatively new class of polymer materials which can show very interesting properties in comparison to the neat polymer matrix, because of the ultra-fine dispersion of inert particles. Actually, the very high surface contact area between the two phases allows an easy and efficient transmission of the stress between the two phases, thus enhancing the beneficial effect of the filler. Mechanical properties,^{1–9} rheological behavior,^{10–19} and permeability^{20–25} are dramatically influenced even by very small amounts of nanofiller.

Creep behavior of nanocomposites has received less attention; moreover, only a marginal part of these papers focus on polymer–clay nanocomposites. In particular, Devasenapathi *et al.*²⁶ studied the creep resistance of low density polyethylene (LDPE)/Cloisite 30B nanocomposites, finding that the creep resistance was enhanced by the addition of nanoclay. This result was attributed to a good exfoliation degree of the nanoclay that restricted the slippage and reorientation of the polymer chains in the matrix.

Dorigato *et al.*²⁷ studied the nonlinear tensile creep of linear low density polyethylene (LLDPE)/fumed silica nanocomposites; more in details, they applied the free volume theory for creep of thermoplastic polymers to construct the generalized creep

curves by applying the tensile compliance-internal time superposition in the non-linear viscoelastic region. They assumed that the nonlinearity is mainly caused by the strain-induced increment of the free volume; then, the strain-dependent shift factors were calculated point by point to superpose compliance curves detected at various stresses, finding that the superposition procedure was possible for both the neat LLDPE and the nanocomposites.

Pegoretti *et al.*²⁸ investigated the tensile mechanical response of polyethylene/clay nanocomposites. They used two different HDPEs with different MFRs (melt flow rates), two organomodified nanoclays and changed the relative amount of polyethylene-*grafted*-maleic anhydride (PE-*g*-MA) compatibilizer. The creep resistance was enhanced by the introduction of clay, with an appreciable dependence on both the polyethylene and the clay type.

Muenstedt *et al.*²⁹ investigated the rheological properties of polymethylmetacrylate (PMMA)/nanoclay systems by creep recovery in shear, finding that while the creep compliances remained nearly unchanged by the filler addition, the recoverable creep compliances were strongly influenced by the addition of the nanoclay in dependence on the volume fraction. This was attributed to a reduction of the macromolecular mobility due to PMMA macromolecules–nanoclay particles specific interaction.

Lv *et al.*³⁰ presented a creep lifetime prediction approach of polypropylene (PP)–nanoclay composites, with and without the addition of polypropylene-*grafted*-maleic anhydride (PP-*g*-MA). They found that nanocomposites with 1 wt % clay experienced an increased deformation and this was attributed to a poor dispersion of the clay in the PP matrix and the slippage of the non-exfoliated clay platelets; on the other hand, 1 wt % clay and PP-*g*-MA significantly improved the creep resistance, due to the enhanced dispersion of clay particles within PP matrix, and demonstrated that both neat PP and nanocomposites undergo a rapid failure when the accumulated strain reaches a critical value, which is found to be independent of the stress level in the temperature range investigated.

Shaito *et al.*³¹ investigated the nonlinear creep response of LLDPE and its nanocomposites with montmorillonite, with and without maleated adhesion promoters. It was found that montmorillonite particles act as hinges in the amorphous matrix and this is reflected in higher modulus, higher yield strain, and increased creep recovery.

Drozdov *et al.*³² performed a study on viscoelasticity, viscoplasticity, and creep failure of polypropylene/clay nanocomposites. Tensile creep tests were carried out at various stresses and room temperature. They found that nanoclay significantly improves mechanical properties and creep resistance, and demonstrated that reinforcement of polypropylene with 1 wt % of nanoclay induces an increase in time to failure by an order of magnitude.

Lietz *et al.*³³ investigated the mechanical and room temperature creep behavior of polystyrene-*block*-polybutadiene-*block*-polystyrene triblock copolymer (SBS) nanocomposites containing different contents of a commercial organoclay prepared by twin-screw extrusion. They found an enhanced creep performance independent on the applied stress level when small amounts of nanoclay were added, while higher clay content only improved the creep performance of the SBS matrix at high stress levels.

Creep behavior of polymer–clay nanocomposites was investigated also with thermoset polymer matrices, instead of the more widespread thermoplastic ones.^{34,35} These studies strongly focused on viscoelastic behavior and modeling issues, also found an enhancement of creep resistance upon adding small amounts of nanoclay.

In general, therefore, the more rigid nanocomposites show a lower compliance and thus they are deformed, under a steady stress, less than the pristine matrix polymer.

From the literature review, it has been found that, to our best knowledge, few data exist on creep behavior of LDPE/clay nanocomposites; more importantly, few information is available on the creep response of these clay-filled nanocomposites under the combined effect of different loads and different temperatures, which are often taken into account separately, as in a mutually exclusive way, while the combined effect of these factors is important to assess the actual behavior of a material subjected to creep deformation.

In this work, therefore, the creep response at different temperatures, as well as the tensile and dynamic–mechanical

response, has been investigated for a LDPE/organomodified clay nanocomposite.

EXPERIMENTAL

Materials and Sample Preparation

The materials used in this work were a sample of film grade (melt index about 3.5 dg/min at 190 °C under 2.16 kg load) polyethylene (Riblene MM20 from Versalis, Italy) and an organo-modified clay sample (Cloisite[®] 15A from Southern Clay Products, Gonzales, Texas, USA). Cloisite 15A (CL15A) is a ditallowdimethylammonium modified montmorillonite with an average equivalent diameter of 8 μm; organo-modifier concentration is 125 meq/100 g clay.

The nanocomposite samples (NLD) were obtained by compounding the LDPE (LD) with the organoclay at 5% (wt/wt) concentration in a Brabender (Germany) PLE330 internal mixer at the temperature of 180 °C and a mixing speed of 50 rpm, for 15 min. Neat polymer was subjected to the same processing.

The specimens (70 mm × 13 mm × ≈0.4 mm) were obtained by cutting them off from compression molded sheets prepared by using a Carver (USA) laboratory press, at 180 °C, pressure about 7 bar and ~3–4 min compression time.

Creep Tests

Creep tests at different temperatures have been performed on all the materials by applying a stress ranging from 1.5 to 3.5 MPa (which are close to the linear elastic zone of the polymer matrix) in a new dedicated apparatus produced by IDEA (Italy). This is basically an oven, equipped with four extensometers, directly connected to mobile clamps and to weight holders. The specimens are mounted between the two clamps and the tests start when the weights are applied at the end of the extensometer. The data are collected and subsequently elaborated in terms of deformation against time. A schematic plot showing the equipment is reported in Figure 1.

Characterization

Mechanical properties in tensile mode were also determined, according to ASTM D638 on specimens (eight for each system) as described in the previous sections, by using an Instron (USA) mod. 3365 universal dual-column machine, with an initial clamp distance of 3 mm and a deformation speed of 1 mm/min (for the first minute of deformation) and then 100 mm/min, in order to perform a more reliable measurement the elastic modulus.

Dynamic mechanical analysis (DMA) was carried out on a 01 dB-METRAVIB (France) DMA50N apparatus, according to ASTM D4065, choosing a heating rate of 5 °C/min up to 100 °C, a strain of 0.05% (after performing an appropriate strain sweep tests, in order to assure not to exceed the limits of the linear viscoelastic range) and a frequency of 1 Hz. Dynamic mechanical tests were performed on specimens (five for each system; thickness ≈ 0.4 mm, width = 5 mm, length = 10 mm) cut off from the compression molded sheets as above.

X-ray diffraction measurements (XRD) were performed, in order to assess the possible intercalation/exfoliation of the nanoclay, on a PANalytical (The Netherlands) Empyrean system

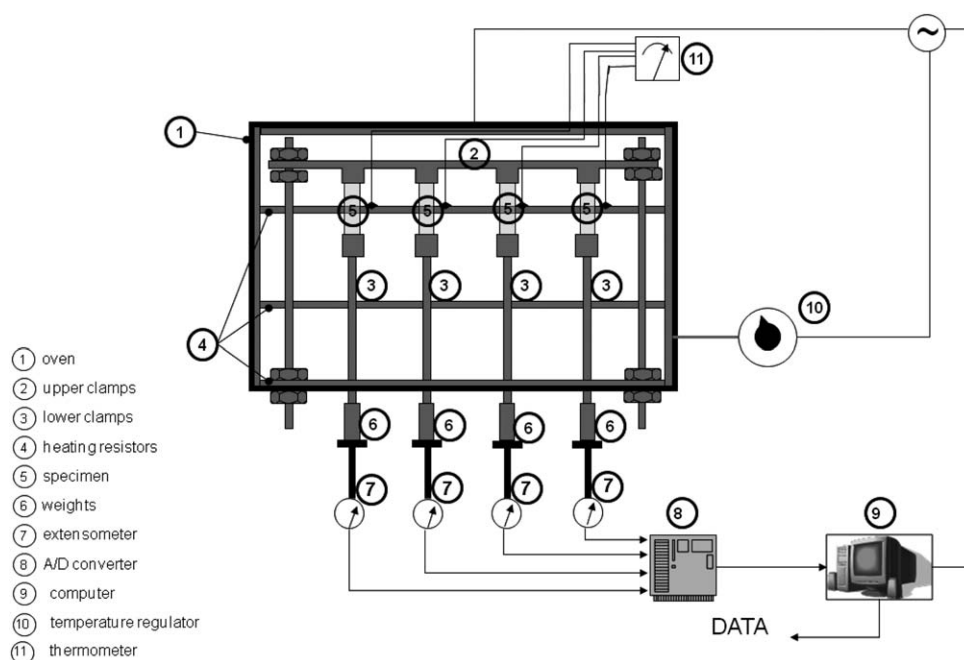


Figure 1. Schematic plot of the creep testing equipment used in this work.

equipped with a PIXcel1D detector. The Bragg–Brentano geometry comprises a Cu X-ray tube (operated at 40 kV and 30 mA; $\lambda = 1.5418 \text{ \AA}$). The patterns were collected in the 2θ range of 2° – 30° , the step size was 0.039° , and the exposure time was 240 s. 2θ angles from the XRD patterns allowed calculating clay interplanar distances (d) through the well-known Bragg's Law, $n\lambda = 2d \sin \theta$ (where $\lambda = 0.154 \text{ nm}$ is the wavelength of the incident radiation and n is a positive integer).

RESULTS AND DISCUSSION

Figure 2 reports the XRD trace of both the clay and the nanocomposite. It can be observed that, following the addition of Cloisite to the polyethylene, 2θ decreases and therefore the interplanar distance of the former increases from its typical

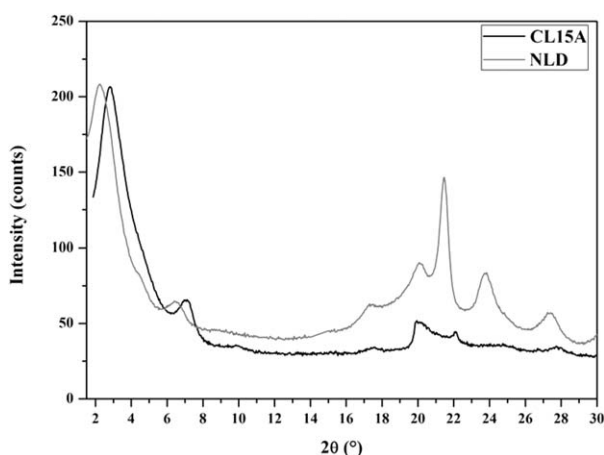


Figure 2. XRD trace of the clay (CL15A) and the nanocomposite (NLD).

value of 3.15 nm to 3.96 nm. This shows that the nanoclay is thus slightly intercalated by the polymer macromolecules.

The main mechanical properties of the two materials are reported in Table I, while the stress–strain curves for some representative samples are reported in Figure 3. The nanocomposite shows a significantly higher value of the elastic modulus (more than 15% increase), while both the tensile strength and the elongation at break decrease. On the other hand, the decrease of the elongation at break is relatively low, and the tensile strength shows only minor variations (\sim by 6%). This last decrease can be attributed just to the decrease of the elongation at break, typical of filled systems. However, this behavior, and in particular the retained ductility of the nanocomposite sample in comparison to the matrix, seems to suggest that a fair dispersion degree of the particles was obtained. These results are in agreement with those of similar systems^{8,9}: the nanoparticles help in increasing the elastic modulus and keeping an almost constant tensile strength, while a slight reduction in the elongation at break occurs; this is typically observed when an intercalated structure is obtained, therefore, also on the basis of the above discussed evidences from XRD analysis, it can be concluded that a moderate intercalation has actually occurred in the prepared nanocomposites.

As regards the results obtained from DMA tests, the $\tan \delta$ curves of the pristine polymer and of the nanocomposite (not reported here for sake of brevity) did not show any transition since the adopted temperature range is above the glass transition temperature and below the melting one; however, with reference to the E' curves (see Figure 4), it was found that the modulus of the nanocomposite is higher than that of the pristine polymer over the entire temperature range here investigated. This means that, even at relatively high temperatures, the

Table I. Tensile Properties of the Two Materials and Storage Modulus at Three Different Temperatures

Sample	Elastic modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	E' (MPa), 30°C	E' (MPa), 60°C	E' (MPa), 90°C
LD	150 ± 6	15 ± 0.5	400 ± 30	325 ± 14	135 ± 6	41 ± 2
NLD	175 ± 8	14 ± 0.6	350 ± 27	384 ± 17	154 ± 8	46 ± 3

nanocomposite keeps a higher rigidity degree and therefore has a higher thermomechanical resistance, in comparison to the pristine polymer, under this load regime.

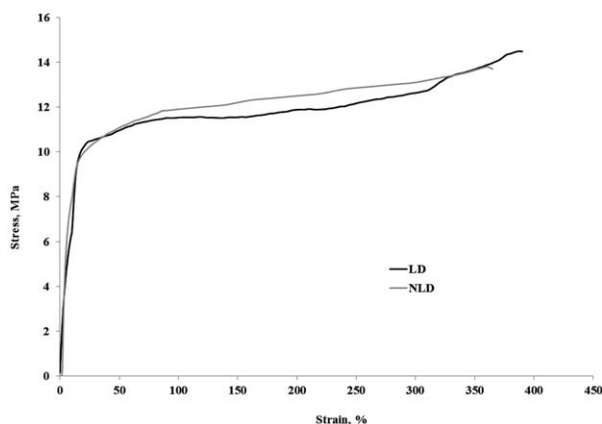
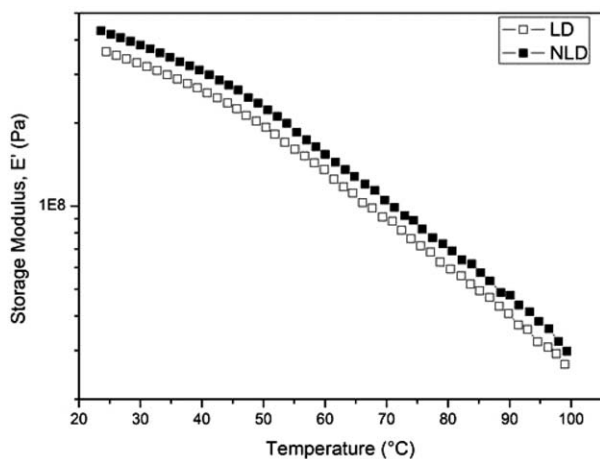
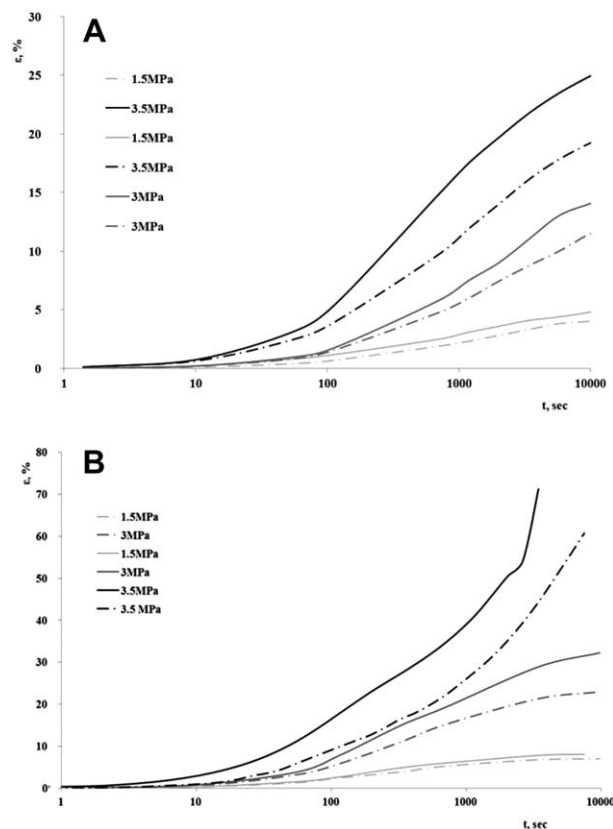
The values of E' at 30°C, 60°C, and 90°C are reported in Table I as well.

The reported values point out and confirm that the nanocomposite has higher thermomechanical resistance in comparison to the pristine polymer, a conclusion which is in agreement with other studies based on different characterization approaches.³⁶

In order to evaluate the actual behavior under steady tensile load, creep tests at different temperatures were carried out. In

Figure 5(a,b), the creep curves of the two systems subjected to three loads at two different temperatures (60 and 80°C, respectively) are reported.

With regard to the creep behavior at 60°C, it can be observed that each system shows the typical trend, although no transition from secondary to tertiary creep can be noticed in the investigated time range. The deformation vs. time of 3 MPa loaded samples is approximately twofold that of the 1.5 MPa loaded samples; however, an additional increase of 0.5 MPa in the applied load leads to a significantly higher deformation, almost twofold the one observed at 3 MPa. In all cases, the nanocomposites show lower deformations in comparison to the pristine polymer; this result is in agreement with that observed during DMA tests. These overall results are in agreement with the findings of other researchers on similar systems^{26,31} and could be attributed to lower macromolecular mobility induced by the presence of clay particles and particularly by the intercalation degree achieved.

**Figure 3.** Stress–strain curves for representative samples of neat pristine matrix (LD) and nanocomposite (NLD).**Figure 4.** Storage modulus of neat pristine matrix (LD) and nanocomposite (NLD).**Figure 5.** Creep curves of the two materials at 60°C (a) and 80°C (b) and at three values of the load. Continuous lines refer to the neat polymer, dotted lines to the nanocomposite.

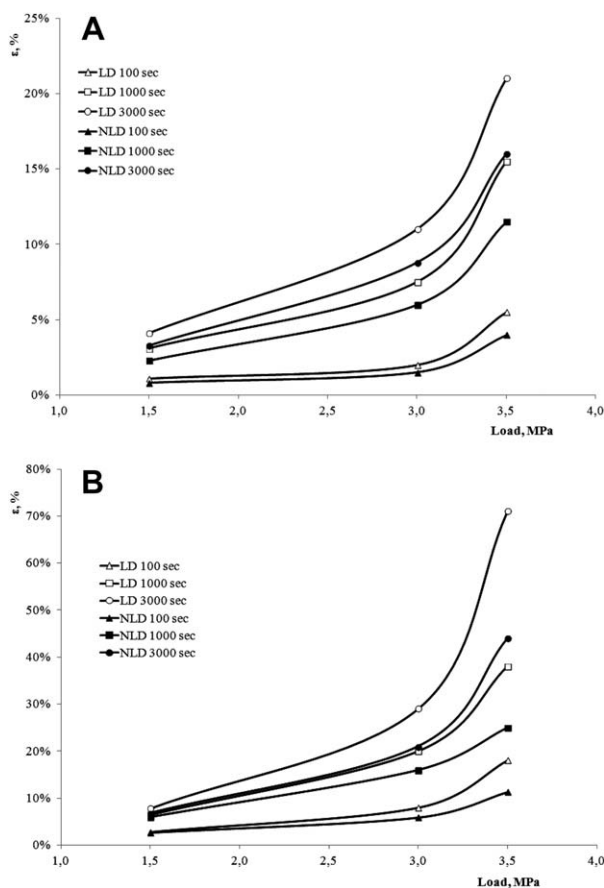


Figure 6. Deformation vs. stress of the two materials at 60 °C (a) and 80 °C (b) and at different time. Empty symbols refer to neat polymer (LD) and full symbols to nanocomposite (NLD).

With concern to the creep curves at 80 °C, the overall trends are in agreement with those found at 60 °C, i.e., with increasing deformation (at given temperature) upon increasing the load, and with the nanocomposites showing lower deformations in comparison to the pristine polymer.

The comparison of the effects related to the two different temperatures clearly points out that significantly higher deformation is achieved at 80 °C. In order to better quantify the differences, Figure 6(a,b) reports the isochronous curves of elongation vs. applied load of the investigated materials at different observation times (i.e., 100, 1000, and 3000 s) for the two temperatures.

As far as the lower temperature is concerned, it can be observed that the differences in the elongation of unfilled polymer and composites are increasing upon increasing either the time or the applied load. When the temperature is taken to higher values, the overall trend is similar; however, on average, the investigated systems seem to be more sensitive on the applied load. In other words, the increase rate of the differences between the unfilled polymer and the nanocomposite is, on average, higher than at the lower temperature. The differences in the creep curves of the two systems are quite large and certainly larger than those shown by the moduli. Of course, this can be ascribed not only to the higher rigidity, but also to the role of the

viscoelastic and plastic components of the deformation,^{27,37–39} that is more important in the unfilled polymer.

CONCLUSIONS

In this work, LDPE/organomodified clay nanocomposites were prepared and subjected to investigation of their dynamic-mechanical and creep behavior at different temperatures and under different loads. The nanocomposite showed a lower creep deformation in comparison to the unfilled polymer matrix, and this behavior has been interpreted in terms of higher rigidity of the nanocomposite and to reduced macromolecular mobility due to the presence of the clay particles and the related intercalated structures, as demonstrated by XRD analysis. This was further proved by DMA tests, which showed higher moduli for the nanocomposites in comparison to the polymer matrix, over the entire temperature range of investigation. The differences in creep behavior between the neat polymer matrix and the nanocomposites were found to be increasing upon increasing the applied load and the temperature, due to the increasing role of the viscoelastic and plastic component of the deformation.

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