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The effects of thermomechanical history and strain rate on antiplasticization of PVC

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Abstract

Antiplasticization is mechanically characterized by an increase in the polymer stiffness and/or yield strength upon the incorporation of a small amount of a low-molecular weight diluent. It is attributed to hindrance of the local β-relaxation motions of the polymer. Here, we have studied the effects of thermal treatment, plastic deformation, and strain rate on the antiplasticization of the yield stress of a 95 wt% poly(vinyl chloride)/5 wt% dioctyl phthalate (PVC/5 wt% DOP) compound. Two thermal treatments were applied to the materials − cooling to room temperature from above T_g by a quench or by a slow oven-cool anneal. When compressed at low to moderate strain rates, antiplasticization was observed in the annealed (physically aged) PVC/5 wt% DOP but not in the quenched (unaged) PVC/5 wt% DOP. Load−unload−reload compression cycles revealed that antiplasticization can be erased by plastic strain; the anomalously high yield stress of PVC/5 wt% DOP observed in the first load cycle softens to a value lower than that of the neat PVC in subsequent cycles. The results indicate that disordered, high free volume microstructural states, obtained either from thermal quenching or from plastic straining, liberate the beta motions of the PVC molecule which, in turn, erase antiplasticization of the yield stress. Earlier work on the rate-dependence of yield has demonstrated that beta motions must be stress-activated in order to yield neat PVC when deformed at high strain rates (>100/s). Hence, we have characterized the rate-dependence of the antiplasticization of the yield stress by testing the annealed materials in uniaxial compression over a wide range of strain rates (10^{-4}/s−3000/s). Antiplasticization was observed in PVC/5 wt% DOP in the low strain rate regime where beta motions are free in neat PVC but hindered in PVC/5 wt% DOP; however, the antiplasticization (elevation of yield stress) gradually diminished with increasing strain rate.

Keywords: Poly(vinyl chloride) (PVC); Antiplasticization; Rate-dependent

1. Introduction

Antiplasticization [1−10] is sometimes observed in diluent-modified glassy polymers; among the manifestations of this phenomenon are anomalously high values of sub-T_g modulus (above that of the undiluted polymer) and enhanced yield stresses. The terminology may be somewhat misleading. The added low-molecular weight diluent increases the global free volume, and thus the glass transition shifts towards lower temperature as expected; however, depending on the molecular size and shape [11] of the diluent molecule, local interactions between the additive and the chain backbone or side groups can suppress sub-T_g relaxations which in turn leads to the need for higher stresses to drive deformation in these antiplasticized compounds. For example, we have recently reported that relatively large, quasi-spherical polyhedral oligomeric silsesquioxane (POSS) diluents lower the T_g of PVC compounds without generating any antiplasticizing effects in the sub-T_g region, whereas a commonly employed plasticizer, dioctyl phthalate (DOP) produced significant antiplasticization [12,13].

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Based on these earlier observations we were interested in examining the robustness of the specific interactions between DOP and PVC that lead to the observed antiplasticization phenomenon. In particular we sought to determine whether or not sufficient energy input (thermal or mechanical) could disrupt these interactions to the point where the antiplasticization phenomenon disappears. Results of this investigation are reported below.

2. Experimental section

2.1. Materials

Custom-made poly(vinyl chloride) (PVC) powder was supplied by Scientific Polymer Products, Inc. (Ontario, NY). The approximate molecular weight of 90,000 g/mol was determined by the supplier. The glass transition temperature of the PVC was 85 °C determined by the tan δ peak in DMA experiments at 1 Hz. Dioctyl phthalate (DOP) was obtained from Sigma–Aldrich. DOP (5 wt%) was incorporated in PVC through melt blending using a lab scale extruder (DACA Instruments microcompounder) at 180 °C. T_g of this compound was 77 °C. The PVC contained 3 wt% thermal stabilizer (Thermolite 890S, Atofina) in order to minimize degradation during processing.

2.2. Compression testing

Uniaxial compression tests were performed over a wide range of strain rates (10^{-4}/s–3000/s) on four pieces of equipment [13,14]: a Zwick mechanical tester (Zwick Roell), an MTS machine (MTS Systems Corporation), a long split Hopkinson pressure bar (Chen Research Group, Purdue University) and a split Hopkinson pressure bar (Boyce Research Group, MIT). Extruded polymer strands were pelletized, compression-molded into disks, and then machined into specimens for compression testing. Right circular cylinder specimens with diameter of 9 mm and height of 4.5 mm were used in tests on the Zwick mechanical tester and the MTS machine, and with diameters of 5 mm and height of 2.5 mm for both split Hopkinson pressure bars (SHPBs). Low strain rate compression testing (10^{-4}/s–10^{-1}/s) was accomplished on the Zwick instrument. To reduce friction, thin Teflon films were placed between specimen and compression platens, and WD-40 lubricant was sprayed between Teflon films and platens. During low rate compression tests, a constant engineering strain rate was applied. Moderate strain rate compression testing was performed on the MTS machine (1/s–50/s) and on the long split Hopkinson pressure bar (150/s–600/s). High strain rate compression testing (700/s–3000/s) was conducted on the smaller split Hopkinson pressure bar apparatus, designed in cooperation with and built by Physics Applications, Inc. (Dayton, OH). SHPB samples were lubricated with a thin layer of petroleum jelly on both surfaces to reduce friction. Results are plotted as the absolute value of true stress vs. true strain, where true strain is defined as the natural logarithm of the current height divided by the initial height, and true stress is defined as the load divided by the current area. Current area is determined based on the initial area and the current strain, using the assumption of incompressible deformation.

3. Results and discussion

3.1. Effect of thermomechanical history on antiplasticization

Two different protocols were employed to reveal the effect of thermal treatment on antiplasticization. Specimens were held at 85 °C for 2 h, and then they were either air-quenched to room temperature or slowly oven-cooled (annealed) by turning off the oven and letting the specimen cool to room temperature over a period of 6–8 h. Fig. 1 shows the effect of these thermal treatments on the stress–strain behavior of undiluted PVC. Annealing physically ages the samples and increases the initial yield stress and the amount of post-yield strain softening; on the other hand, quenching results in a lower yield stress [15]. Both thermal histories lead to pure PVC materials that exhibit substantial strain softening and subsequent plastic deformation after yield, eventually leading to convergence of the PVC stress–strain behavior at the highest levels of deformation.

Fig. 1 also compares the true stress–true strain curves of neat PVC and PVC diluted with 5 wt% DOP after the two different thermal treatments. Antiplasticization was observed in the annealed PVC/5 wt% DOP specimens as evidenced by anomalously high yield stress. We hypothesize that the 2 h/85 °C heat treatment is sufficient to disrupt the antiplasticizing DOP–PVC interactions that are present in the as-compounded material. The evidence in Fig. 1 indicates that these interactions are regenerated during the slow 6 h cooling cycle, leading to the highest observed yield stress among the materials studied. However, antiplasticization was not observed in the quenched PVC/5 wt% DOP; local constraints on sub-T_g beta

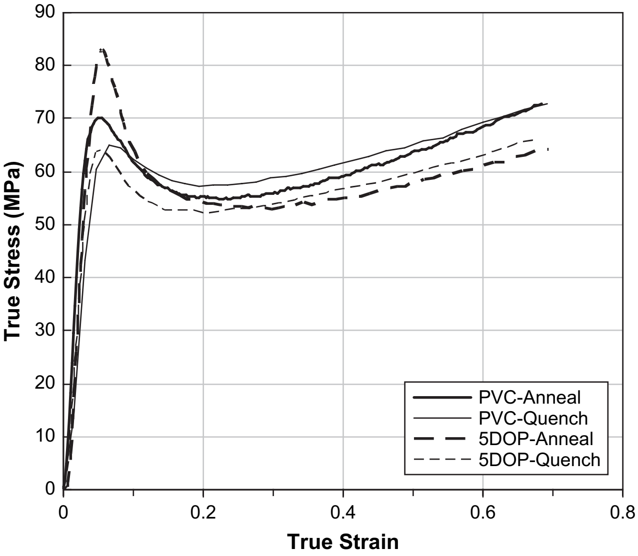

Fig. 1. True stress–true strain curves of PVC and PVC/5 wt% DOP: annealing vs. quenching.

chain motions that produced the enhanced yield stress are released during the 2 h/85 °C heating, and do not have sufficient time/mobility to reform in the quenched sample which has a correspondingly low yield stress.

After strain softening, both the annealed and quenched PVC/5 wt% DOP exhibit lower flow stresses than the neat PVC (Fig. 1). Because steady plastic deformation is known to bring the material to an internal structural state that is essentially equivalent to that which exists at the material's T_g [16], it is expected that the 5 wt% compounds, which are deforming at a higher effective temperature, should exhibit a correspondingly lower flow stress. Therefore, the unusually large magnitude of strain softening observed here for the annealed PVC/5 wt% DOP sample results from a combination of two effects: liberating the antiplasticization constraints on local chain motions as well as the free-volume-based rejuvenation effect of plastic deformation in glassy amorphous polymers. Conversely, the absence of any enhancement of strain softening in the quenched PVC/5 wt% DOP compound indicates that the heating/quenching history effectively 'erased' the antiplasticization constraints that had been present in the material.

In order to examine further the effect of inelastic strain on antiplasticization, annealed PVC and PVC/5 wt% DOP samples were first loaded in compression to a true strain of −0.15, unloaded, and then immediately reloaded until the true strain reached −0.7. Fig. 2 shows the true stress–true strain curves of PVC and PVC/5 wt% DOP in this two-cycle compression testing at 0.001/s. While the PVC/5 wt% DOP material exhibited antiplasticization (enhanced yield stress) in the first loading (c1), no antiplasticization was observed in the reloading curve (c2). This observation indicates that the initially restricted local motions in PVC/5 wt% DOP were liberated by the inelastic deformation in the first loading step and that this altered structural state is retained at room temperature after unloading. This result demonstrates that, while plastic deformation liberates the sub-T_g chain motions and thereby erases the antiplasticization, active plastic flow is not required to retain this new state. That is, plastic deformation followed by unloading at 20 °C irreversibly breaks the associations between DOP and the PVC chains that had previously restricted the sub-T_g relaxations to produce an antiplasticized compound. This result is fully consistent with the previous observation (Fig. 1) that antiplasticization is erased in the heated and quenched PVC/5 wt% DOP material.

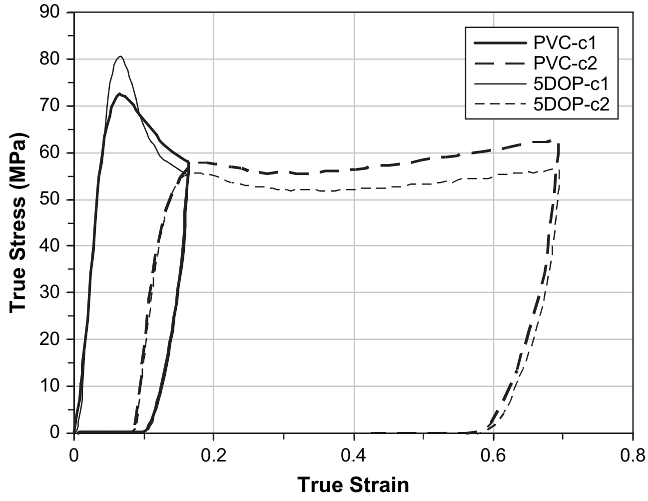

Fig. 2. True stress–true strain curves of PVC and PVC with 5 wt% DOP under uniaxial compression at 0.001/s. Samples were compressed to a true strain of −0.15 (c1), unloaded, and then immediately reloaded to a true strain of −0.7 (c2).

3.2. Rate-dependence of antiplasticization

Fig. 3a presents the true stress–true strain curves of annealed PVC and PVC/5 wt% DOP at strain rates of 0.001/s, 1/s, 200/s, and 2000/s; the resulting values of yield stress are summarized in Fig. 3b. (Adiabatic heating at high strain rates leads to significant post-yield thermal softening at 200/s and

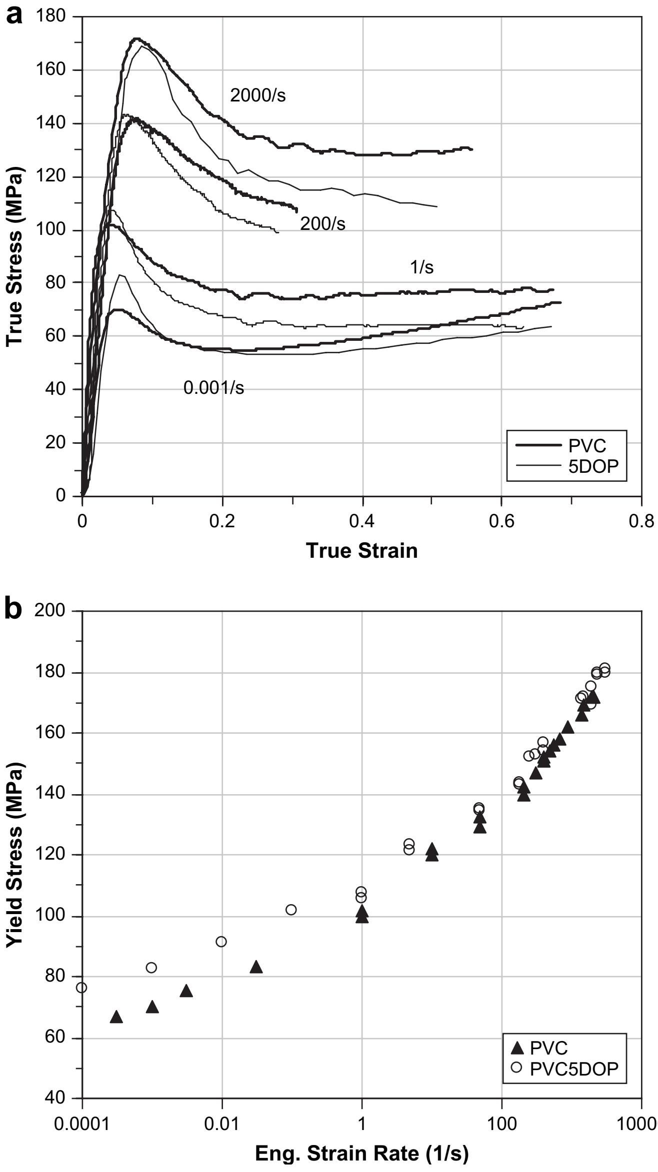

Fig. 3. Rate-dependence of antiplasticization in PVC and PVC/5 wt% DOP under uniaxial compression: stress–strain behavior at various strain rates (a) and yield stress as a function of engineering strain rate (b).

2000/s in additional to the strain softening seen at low rates, but the values of yield stress are unaffected by this complication [17].) For unmodified PVC, the yield stress increases with the logarithm of strain rate with a clear trend towards increased rate sensitivity at higher deformation rates. Antiplasticization is clearly seen in Fig. 3 for the PVC/5 wt% DOP compound only at low strain rates. In this low rate regime, neat PVC, in which beta motions are not restricted by any antiplasticizing interactions, exhibit lower values of yield stress than the DOP-containing compound. Above about 100/s, a non-negligible stress is also required to activate the β-process in the unmodified PVC [13]. Eventually at high enough strain rates the behavior of the two materials converges (Fig. 3b) and any observable influence of antiplasticization on the yield stress disappears; at very high rates the beta motions require full stress activation in both the PVC and the PVC/5 wt% DOP.

4. Conclusions

Antiplasticization is observed in PVC compounds containing low amounts of DOP diluent. Here, this phenomenon was revealed in the large deformation behavior in the context of enhanced yield stresses, enhanced strain softening and altered rate sensitivity of the yield stress. Heating the PVC/5 wt% DOP compound to 85 °C followed by quenching erased the antiplasticization; plastic deformation followed by rapid release of the stress at room temperature produced the same effect.

In compression testing over a wide range of strain rates (10^{-4}/s–3000/s), the PVC/5 wt% DOP exhibited higher yield stresses (antiplasticization) than the neat PVC in the low rate regime, and this antiplasticization phenomenon gradually disappeared with increasing strain rate.

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