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Softening and melting mechanisms of polyamides interfering with sliding stability under adhesive conditions

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Abstract

The thermal stability of polymers is a main issue when used as friction elements under dry sliding. Cast polyamide grades processed with either natrium or magnesium catalysors are slid on a small-scale and a large-scale test configuration to reveal the effect of softening or degradation on the sliding stability and to investigate possibilities for extrapolation of friction and wear rates between both testing scales. The combination of softening and afterwards transition into the glassy state is detrimental for the sliding stability of natrium catalysed polyamides, characterised by heavy noise during sliding. A transfer film formed under continuous softening also provides high friction. Melting during initial sliding is necessary for stabilisation in both friction and wear, and eventual softening of a molten film near the end of the test then not deteriorates the sliding stability. Softening of magnesium catalysed polyamides is favourable for the formation of a coherent transfer film resulting in more stable sliding than natrium catalysed polyamides. The differences in softening mechanisms of both polyamide grades is correlated to structural changes investigated by thermal analysis and Raman spectroscopy: the γ crystalline structure prevails in magnesium catalysed samples and the α crystalline structure is predominant in natrium catalysed samples. For internal oil lubricated polyamides, a time dependent degradation of the polyamide bulk deteriorates the supply of internal oil lubricant to the sliding interface, resulting in high friction and wear under overload conditions. As the degradation mechanisms during sliding are strongly correlated to the test set-up, extrapolation is only possible for friction in a limited application range, while wear rates cannot be extrapolated.

Keywords: Polyamide; Crystallisation; Raman spectroscopy

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1. Introduction

Polymers are used for dry sliding applications as relatively soft materials with self-lubricating properties. The resistance against sliding is characterised by a horizontal friction force depending on normal load and sliding velocity. The friction and wear properties change, however, due to transfer of wear debris and formation of a polymer film on the steel counterface, often providing low friction and low wear rates.

Most of the mechanical energy consumed in the course of friction is transformed into heat, leading to a rise in temperature on the rubbing surfaces [1]. Degradation as softening, melting, oxidation and pyrolisis may therefore take place easily on the polymer surface and these processes further control the sliding stability [2–5]. In some cases as, e.g. for ultra high molecular weight polyethylene (UHMWPE), softening under high loads is favourable for stable sliding [6]. Other polymers as, e.g. polyamides (PA) are, however, prone to overload and fracture [7]. Additives as oil or solid lubricants into the polyamide matrix improve the sliding stability, although it is not clear for those composites how the performance of fillers is affected by softening or melting of the bulk material.

The energy dissipation depends on the test-layout and as tribological testing is mostly done on a standardised pin-on-disc or bloc-on-ring tester, the performance under real working conditions may differ from the situation on laboratory scale. Also the sample area has a role in the energy dissipation and mainly for filled polymers, the supply of internal lubricant from the polymer bulk into the sliding surface is improved for large sliding areas. Besides applied normal loads and sliding velocities, degradation mechanisms are influenced by the testing scale. The practical application range of a sliding material is often characterised by a limiting

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pv (pressure–velocity) value that is closely related to an acceptable wear rate at a certain temperature. In some cases, this limit can, however, be exceeded while the polymer still performs low friction and wear due to surface softening. Extremely high load conditions typically apply for design of bearing elements [8]. Extremely high sliding temperatures typically apply for processing of polymer melts [9]. The aim of this paper is:

- to reveal differences between degradation by softening and/or melting during sliding,
- to compare degradation mechanisms on both small-scale (low load/high velocity) and large-scale (high load/low velocity) sliding tests and analyse whether a small-scale test at high temperature can be extrapolated to large-scale tests at high load,
- to explore the polyamide performance under overload conditions,
- to explain differences in softening mechanisms and sliding stability by differences in polymer structure.

2. Experimental

2.1. Test materials

Three cast polyamide types are used as sliding material, i.e. pure polyamide that is natrium catalysed (PA–Na), pure nylon that is magnesium catalysed (PA–Mg) and polyamide PA–Na with a homogeneous dispersion of oil added during the casting process (PAo1). Mechanical parameters of the different grades are shown in Table 1 [10]. They are produced by Quadrant EPP by low pressure monomer casting, allowing for low process temperatures and polymerisation of molten lactam monomers right in the heated mould under atmospheric pressure. Characteristics of the polymerizing reaction during casting, such as initiation and propagation mechanisms, have been discovered with adding sodium as an activator, diisocyanates as a chain initiator and Na or Mg as a catalysor from liquid steams [11,12]. According to Kang et al. [13], the dispersion of oils becomes inhomogeneous in nylon for contents above 8 wt%. Test samples are machined from the bulk of cast elements, in order to avoid edge effects causing eventual inhomogeneities.

The counterfaces consist of cold rolled steel 42 CrMo4 (DIN 1.7225) with hardness 330 HV, yield strength $R_e = 765\ \mathrm{N/mm^2}$, tensile strength $R_m = 980–1180\ \mathrm{N/mm^2}$ and chemical composition (wt%): $C = 0.38–0.45$, $Si < 0.40$, $Mn = 0.60–0.90$, $P < 0.035$, $S < 0.030$, $Cr = 0.90–1.20$, $Mo = 0.15–0.30$. Before each test, the surfaces were ground to an average surface roughness $R_a = 0.20\ \mu m$ measured parallel to the sliding direction and $R_a = 0.60\ \mu m$ perpendicular to the sliding direction. These values are representative for mainly an adhesive friction and wear type. Roughness is measured on a two-dimensional Perthen 5 SP according to DIN 4768. Prior to each test, polymer and steel surfaces were cleaned with acetone.

2.2. Sliding test equipment

Small-scale tests are done with a polymer cylinder (diameter 6 mm, length 12 mm) reciprocating sliding against a fixed steel counterface (58 mm × 38 mm). The polymer specimen is mounted by means of a clamp and center mechanism in a moving fixture, which provides an oscillating motion by a controlled variable speed motor through an eccentric power transmission for the adjustment of the stroke. A line contact is presently chosen for simulation of high contact pressures and easy alignment of the sliding pair. The steel counterface is connected to a base plate by means of four leaf springs with high stiffness in vertical direction and appropriate flexibility in horizontal direction. A normal load is manually applied through a spring and lever system that pulls down a bridge system over the polymer specimen. Contact between the bridge and the moving fixture is made by a roller bearing. A piezo-electrical force transducer with maximum capacity of 500 N in contact with the stationary steel plate is used to measure the horizontal reaction force that the polymer specimen exerts on the counterface. The counterface temperature can be controlled by means of resistance heating through four Vulstar cartridges.

A large-scale flat-on-flat tribotester is needed for investigating the effect of overload on large contact areas, related to the practical application of polyamides as bearing material possibly acting under yielding conditions. Two stationary polymer wear samples (150 mm × 150 mm) are mounted on top and bottom of a horizontally stiff frame and are in contact with the steel counterfaces (410 mm × 200 mm) that are positioned on top and bottom of a central sliding bloc. The latter moves reciprocating through the centre of the machine in contact with the polymer samples and is loaded by a vertical jack with maximum capacity of 6500 kN. Two dynamometers with maximum capacity of 2500 kN are in contact with the sliding bloc for recording the horizontal forces. The sliding velocity is controlled by a hydraulic circuit.

Table 1
Mechanical properties of different polyamide grades (23 °C/60% RH)

	Test material	d (g/cm^3)	E (MPa)	σ_y (MPa)	ε (%)	Compressive stress (MPa) at nominal strain		
						1%	2%	5%
PA–Na	Pure nylon Na catalysed	1.150	1700	55	>50	26	51	92
PA–Mg	Pure nylon Mg catalysed	1.150	1500	75	>50	23	42	82
PAo1	Homogeneous oil dispersion	1.135	1450	45	>50	22	43	79