Tribology International 43 (2010) 289–298

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

Rolling and sliding wear properties of hybrid systems composed of uncured/cured HNBR and partly polymerized cyclic butylene terephthalate (CBT)

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ARTICLE INFO

Article history:
Received 2 April 2009
Received in revised form
4 June 2009
Accepted 11 June 2009
Available online 17 June 2009

Keywords:
Rubber
Hybrid compound
Rolling and sliding wear
Wear mechanisms

ABSTRACT

The phase structure, rolling and sliding wear properties of the hybrids composed of uncured/cured hydrogenated acrylonitrile/butadiene rubber (HNBR) and partly polymerized cyclic butylene terephthalate oligomers (CBT) were investigated. The ratio between HNBR and CBT was varied in the hybrids between 1:0.5 and 1:2. The CBT conversion and phase structure were studied by extraction, differential scanning calorimetry, and dynamic-mechanical thermal analysis.

The rolling and sliding wear behaviors of the hybrids under unlubricated condition were determined by using various wear test rigs. It was found that the partly polymerized CBT worked as reinforcement in the HNBR matrix. The specific wear rate of the compounds usually decreased with increasing amount of CBT in both rolling and sliding wear tests. The coefficient of friction (COF) of the hybrids strongly depended on the type and configuration of the wear tests. Dynamic vulcanization of the HNBR in the HNBR/CBT mixes mostly improved the tribological performance. The wear mechanisms were studied as a function of CBT content and discussed.

1. Introduction

Rubber/thermoplastic combinations offer various benefits, e.g. cost efficiency (thermoplastics are normally cheaper than rubbers), property improvements (e.g. chemical and thermal resistance), easy recycling (e.g. via remelting). Rubber/thermoplastic hybrids often possess attractive tribological performance making them suitable for engineering applications. Some research work has already addressed the tribology of rubber/thermoplastic blends and thermoplastic dynamic vulcanizates (e.g. [1–3]). A very promising new option is to combine rubbers with cyclic butylene terephthalate oligomers (CBT). Note that CBT can be polymerized above its melting ($T \approx 140$–$150\,^{\circ}$C) into polybutylene terephthalate (pCBT). This temperature range is closely matched with that of rubber curing. Moreover, the polymerization temperature and time of CBT can be adjusted to the requirements by selecting suitable catalysts [4,5]. The designation pCBT considers that its properties (molecular mass, crystallinity, ductility) somewhat differ from those polybutylene terephthalates which have been produced in traditional polycondensation processes.

CBT can work as active filler in cured rubbers when partly or fully polymerized (designated further on by (p)CBT and pCBT, respectively). It was reported that the stiffness and the strength of the related hybrids are highly enhanced compared to the parent rubber [6,7]. In addition, the CBT acts as viscosity reducer for the parent rubber mixes. Preliminary results on the tribological properties of such hybrids with cured hydrogenated acrylonitrile/butadiene rubber (HNBR) were very encouraging [7]. Note that HNBR is preferentially used in demanding engineering applications (seals, membranes, transmission belts, hydraulic hoses, vibration dampers, etc. [8]) in which heat-, oil- and wear-resistance [9,10] are primary requirements.

The aim of this work was to check whether the (p)CBT modification of uncured and dynamically cured HNBRs is a straightforward strategy to improve the wear resistance of the related hybrids. Accordingly, in this paper the rolling and sliding friction and wear of HNBR based compounds containing partly polymerized CBT were studied against steel in various testing configurations. The HNBR itself was uncured or fully cured (unHNBR and curedHNBR, respectively). The ratio of unHNBR:(p)CBT was 100:50, 100:100, 100:150 and 100:200, respectively, whereas for the cured mix the ratio 100:100 was selected. The rolling/sliding tests covered orbital rolling ball (steel)-on-plate (rubber) (orbital-RBOP), pin (steel)-on-plate (rubber) (POP), roller (steel)-on-plate (rubber) (ROP) and oscillating cylinder (steel) on plate (rubber) (fretting) configurations under unlubricated condition. Extraction, differential scanning calorimetry (DSC) and dynamic-mechanical thermal analysis (DMTA) were adopted to clarify the CBT conversion to pCBT, and

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doi:10.1016/j.triboint.2009.06.008

to get a deeper understanding in the phase structure of the hybrid compounds. The coefficient of friction (COF) and the specific wear rate (W_s) were determined. The worn surfaces were investigated in scanning electron microscope (SEM) and white light profilometer and the related wear mechanisms were analyzed.

2. Experimental

2.1. Preparation of unHNBR– and curedHNBR–(p)CBT

Before mixing the cyclic butylene terephthalate (CBT® 160, Cyclics Europe, Schwarzheide, Germany) with the hydrogenated acrylonitrile/butadiene rubber (Therban® LT VP/KA 8882 of Lanxess, Leverkusen, Germany; acrylonitrile content: 21%, Mooney viscosity ML(1+4)100 °C = 74), the CBT and HNBR have been dried separately in an oven (Heraeus UT-20; Thermo Fisher Scientific Inc., Schwerte, Germany) at 80 °C under vacuum overnight. The HNBR/CBT ratio in the corresponding recipes was: 100/50, 100/100, 100/150 and 100/200 (part/part), respectively. Their compounding was done as described below. First, HNBR was put in a laboratory kneader (50 cm^3, type: Brabender Plasticorder 814600, Brabender, Duisburg, Germany) and mixed at 190 °C for 3 min. The revolution of the kneaders was 30 min^{-1}. Afterwards the CBT was added and the mixing process lasted for 30 min at the same temperature. The overall mixing time should have been enough to trigger the polymerization of CBT [6,7,11]. Because the HNBR did not contain curatives it has not been cured in the related mixes. The mixes, dried overnight under the same condition as the parent HNBR and CBT, were hot pressed (Collin P 200 E press; Dr. Collin GmbH, Ebersberg, Germany) at 230 °C for 5 min into ca. 2 mm thick sheets. The obtained hybrids are referred to as unHNBR–(p)CBT 100–50, –100, –150 and –200, respectively. "Un" reflects that the HNBR was uncured, while "(p)CBT" means that the CBT was partly polymerized. The digits in the designations represent the content (in part) of the HNBR and CBT, respectively. The arithmetical surface roughness (R_a) of the tested rubber sheets was between 1.2 and 2.0 μm.

The composition of cured HNBR–(p)CBT 100–100 was: HNBR 100 part, CBT 100 part, di(tert-butylperoxyisopropyl)benzene (Perkadox 14S-Fl, Akzo Nobel, Düren, Germany) 3 part, triallyl cyanurate (Perkalink 300-50d, Akzo Nobel) 3 part, ZnO 2 part and MgO 2 part. The curatives were introduced in the HNBR/CBT blend after 20 min of mixing at $T = 190$ °C. Dynamic vulcanization of the HNBR occurred during 10 min additional mixing. "Cured" in the sample designation means that HNBR was dynamically cured (i.e. during melt mixing) in the presence of the peroxide curatives. 2 mm thick sheets were gained by the same hot pressing technology adopted for the unHNBR–(p)CBT series.

2.2. Testing

2.2.1. Extraction

Because chloroform can dissolve only unpolymerized CBT (and does not attack polymerized one), it was chosen as solvent for extraction. However, it is noticeable that uncured HNBR dissolves partly in chloroform, too. This has been considered when calculating the CBT conversion.

The samples of the unHNBR–(p)CBT series and curedHNBR–(p)CBT 100–100 were wrapped by filter paper and kept in chloroform for 3 days at room temperature. Afterwards, the samples together with the wrapping filters were dried in a ventilation cabinet for 3 days at room temperature. The mass loss was calculated by considering the mass of the samples before and after extraction.

2.2.2. Differential scanning calorimetry

DSC traces were registered in a DSC device (DSC821e of Mettler Toledo, Giessen, Germany) under nitrogen purging in a temperature range from 25 to 250 °C at heating and cooling rates of 10 °C/min.

2.2.3. Dynamic-mechanical thermal analysis

DMTA spectra were measured on rectangular specimens in tensile mode at a static preload 0.01 N with a superimposed sinusoidal 0.01% strain. The frequency was 10 Hz and the spectra were registered in a broad temperature range (from −100 to +240 °C) with a Q800 device of TA Instruments (New Castle, DE, USA). From −100 °C, the temperature was increased by 5 °C and stabilized for 3 min for each step.

2.2.4. Density determination

For the density determination the Archimedes principle (buoyancy method with water) was adopted according to the ISO 1183 standard.

2.3. Rolling and sliding

2.3.1. Testing

The unlubricated rolling friction and wear of the composites were evaluated in an orbital rolling ball (steel)-on-plate (rubber) test configuration. The rubber sheet was worn by a steel ball (100Cr6, diameter: 14 mm, arithmetical surface roughness R_a: 1 μm), which rolled along a circular path (diameter: 33 mm) when pushed by a given normal load against the rubber sheet. The parameters set for this configuration were: normal load 90 N, revolution 280 rpm, duration 3 h.

Sliding friction and wear characteristics were assessed in pin (steel)-on-plate (rubber), roller (steel)-on-plate (rubber) and oscillating cylinder (steel) on plate (rubber) (fretting) tribotests under dry condition.

The POP rig was fixed in a Wazau device (Berlin, Germany). In this test setup a steel pin (100Cr6, $R_a < 1$ μm) with a hemispherical head of 10 mm diameter rotated along a circular path of 33 mm diameter. The pin was pressed on the rubber plate with a defined load. The following parameters were chosen for this configuration—normal load 2 N, sliding speed 250 mm/s, duration 90 min.

In ROP, a self-rotating steel roller (9SMnPb28k, diameter: 10 mm, width: 20 mm, $R_a \approx 0.9$ μm) was pressed against a rubber strip of 8 mm width in a SOP 3000 tribotester (Dr Tillwich GmbH, Horb-Ahldorf, Germany). The test parameters were as follows: normal load ≤2 N, sliding speed 250 mm/s and duration 90 min.

In the fretting tribotest, a steel cylinder was pushed by a defined normal load and oscillated on the surface of the fixed rubber specimen. The diameter and the contact length of the cylinder ($R_a \approx 0.9$ μm) were 15 and 10 mm, respectively. The applied experimental parameters were: normal load ≤10 N, frequency of the oscillation 10 Hz, stroke 3 mm and duration 90 min.

All the above test rigs allowed us to monitor the dynamic coefficient of friction as a function of time.

The specific wear rate (W_s) was calculated according to

$$W_s = \frac{\Delta V}{F_N L} \tag{1}$$

where ΔV (mm^3) is the volume loss, F_N is the normal load, L (m) is the overall rolling/sliding distance. The loss volume (ΔV) was calculated by measuring the depth and width of the wear tracks by white light profilometer (see later) and supposing the shape of the wear track is a half-ellipse.

The schemes of the above testing methods are depicted in Fig. 1.