Beamline: BM28

Proposal number: A28-1-1262 **Date of experiment:** 20/4/22 – 25/4/22

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Investigating the strain-induced crystallisation behaviour of self-healing natural rubber vulcanizates

INTRODUCTION

Vulcanised natural rubber (NR), used in vehicle tyres, has excellent resilience and mechanical properties e.g. tensile strength, elasticity and tear resistance. The mechanical properties of NR are linked to the molecular orientation and strain-induced crystallization (SIC) behaviour of its three-dimensional covalent network structure. Yet, this structure inhibits NR from being reprocessed or recycled. Therefore, developing a new generation of vulcanised rubbers with balanced mechanical strength and self-healing properties is vital. To address this challenge, we have developed a new set of self-healing rubber-carbon black (NR/CB) composite materials which have comparable mechanical properties to NR. This beamtime investigated the SIC behaviour of several NR/CB composites showing how the mechanical properties can be correlated with the crystalline micromorphology changes during drawing.

EXPERIMENTAL

X-ray measurements on BM28, were obtained using a wavelength $\lambda = 1.033$ Å and a beam spot size of 138 µm × 70 µm. The 2D WAXS data was collected on the Pilatus 1M detector, positioned at a distance of 276 mm from the sample. A set of four NR/CB composite samples were prepared (at 40 pph loading), with different commercial CB particles with increasing size order (average particle size in nm), namely NR/135 (22 nm), NR/234 (25 nm), NR/330 (29 nm) and N660 (50 nm), these were compared with a NR control sample (unfilled), denoted as CV-ZS. Dumbbell samples were drawn at ambient temperature using a Linkam TST350 tensile testing instrument (200 N load cell), positioned vertically in the X-ray beam, at a rate of 60 µm/s to a maximum elongation on 400% (see Figure 1). Throughout the draw, 2D WAXS patterns were obtained at a frame rate of 1 s with a dead time then of 9 s (overall 10 s intervals).

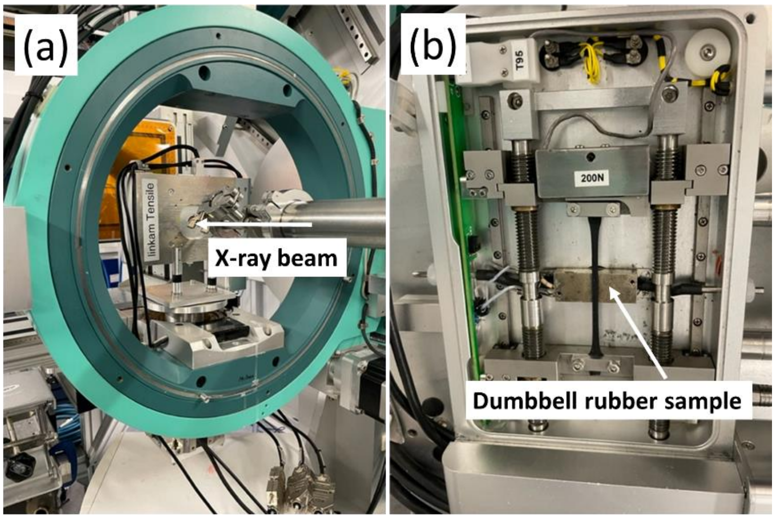

Figure 1. (a): Linkam TST350 tensile testing positioned on the beamline. (b): Rubber sample in the tensile tester drawn to 400%.

RESULTS AND DISCUSSION

The strain-induced crystallization (SIC) of the NR/CB composites was monitored in-situ (at ambient temperature), and mapped on to the tensile testing curves. The stress-strain curves (up to 400% strain), are given for the NR/CB composites and control NR sample without CB filler (CV-ZS), in Figure 2(a). In the stress-strain curves shown, the addition of CB has a reinforcing effect on the mechanical properties of NR. The upturn of the stress in all NR/CB composites occurs at lower stress compared with the unfilled (CV-ZS) rubber. From the NR/CB samples the NR/330 composite shows the greatest difference in stress-strain behaviour, with NR/135 having the next largest effect. In Figure 2(b), the 2D WAXS patterns are plotted at various strains (between 50 – 400%) on an example stress-strain curve for NR/135. The onset of crystallization is seen in the NR/CB composites at around 200% strain. Investigating the SIC further, analysis of the 2D WAXS patterns is necessary, focusing on the strain region when SIC commences and at its maximum of 400% strain.

Figure 3(a), shows the 2D WAXS patterns for all NR/CB composites between 150% - 400% stain (note the draw direction is vertical in all patterns). The patterns at 150% mainly show an isotropic amorphous halo which indicates an unoriented network of rubber chain and that SIC has not yet started. At a strain of 200%, various oriented crystalline arc shaped reflections start to develop, and at 400% these crystalline reflections are clearly evident in all NR/CB composites. However, there is still evidence of the amorphous unoriented halo at 400%, indicating there is still a significant amount of unoriented rubber chains coexisting in the rubber matrix. Note, that in previous studies NR without filler shows the onset of SIC at higher strains of ~400%.

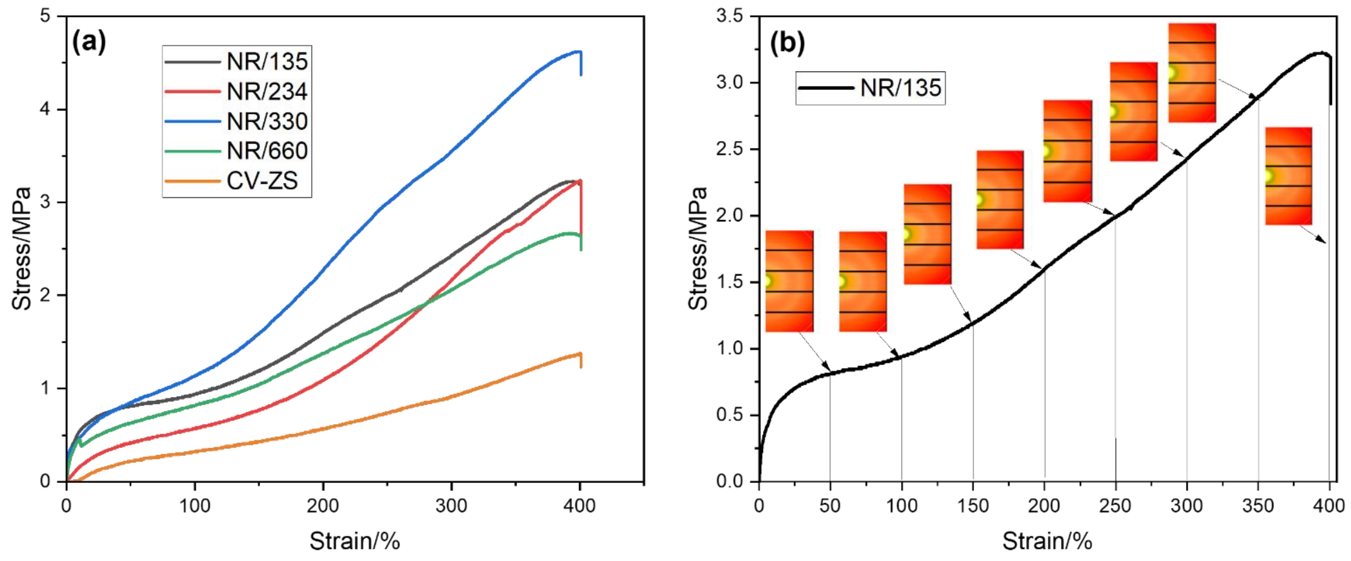

Figure 2. (a): stress-strain curves at ambient temperature, for all NB/CB composites and CV-ZS.
(b): stress-strain curve for NR/135 including corresponding 2D WAXS patterns at specific strains between 50 – 400%.

In Figure 3(b), the 2D WAXS patterns at 400% strain are shown for NR/135, NR/330 and unfilled rubber CV-ZS. Here, the crystalline peaks are indexed as the (200), (201) and (120) which are assigned to the monoclinic unit cell for natural rubber. From the 2D WAXS patterns at 400% the NR/135 and NR/330 composites show the clear development of the crystalline peaks in contrast with CV-ZS which shows little crystalline peak development at this strain.

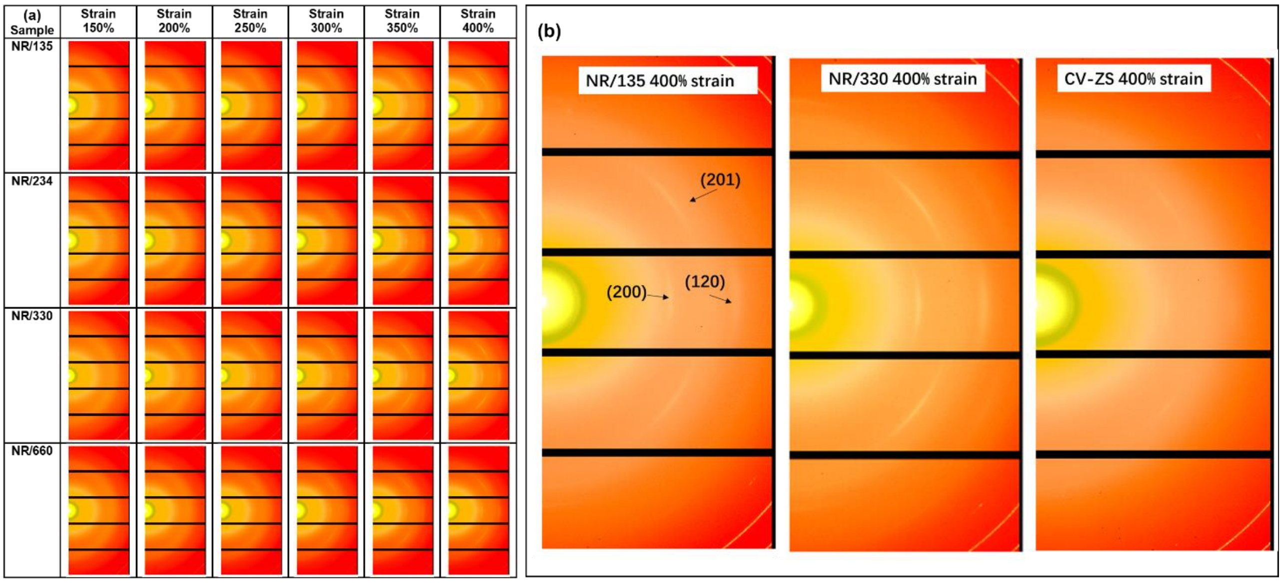

Figure 3. (a) 2D WAXS patterns for all NR/CB composites from a strain of 150% to 400%. (b) expanded 2D WAXS patterns at 400% strain for NR/N135, NR/330 and unfilled rubber CV-ZS. The draw direction is vertical in all patterns.

CONCLUSIONS

Here, we have sown that the addition of CB filler in NR not only has a reinforcing effect the mechanical properties, but strain-induced crystallization commences at lower strains compared with the unfilled NR. A publication of the full results can be found in [1].

[1] Understanding the dynamic network recovery ability of natural rubber/carbon black nanocomposites. Tian Xia; Alan M. Wemyss; Reza Salehiyan; Ellen L. Heeley; Xiao Hu; Zaifeng Tang; Yuchen Sun; Darren J. Hughes; Tony McNally. Submitted to Advanced Composites and Hybrid Materials, August 2023.