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The glass transition, segmental relaxations and viscoelastic behaviour of particulate-reinforced natural rubber

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ABSTRACT

The role of filler particles in defining local changes to the dynamics of elastomer polymers – specifically in relation to the reinforcement of commercial elastomer systems – is as yet incompletely resolved. This work examines the glass transition of filled, crosslinked natural rubber in relation to filler reinforcement mechanisms using a variety of complimentary experimental techniques. Carbon black and precipitated silica filler particles with a wide range of surface areas, structures and surface activities are used as the reinforcing phase. No effect of the filler particles on the calorimetric glass transition is observed in terms of shifting, broadening or transition strength. Dielectric spectroscopy measurements show that the polymer relaxation times of the filled rubbers in the glass-to-rubber transition zone remain essentially equivalent to that of the corresponding unfilled material. Dynamic mechanical analysis demonstrates that the storage moduli of the filled elastomers are significantly amplified on the rubbery side of the glass transition. Elastic stiffening mechanisms are discussed in the context of contributions from filler networking. The reason for a distinct lack of evidence for filler-induced polymer modification may be due to the nature of polymer confinement associated with the imperfect dispersion state of the fillers in the sample and the fact that the fillers themselves are formed from aggregated primary particles rather than being true nanoparticulates.

1. Introduction

Crosslinked rubbers (elastomers) reinforced with carbon blacks and precipitated silicas are a widely used and well established type of high performance composite material. However the precise mechanisms of filler reinforcement of elastomers remain incompletely understood despite the large scale utilisation of filled elastomers for a wide range of safety–critical engineering applications. A particularly industrially important aspect of reinforcement is the modification of the strain-dependent viscoelastic spectrum of the elastomers imparted by the presence of the filler phase. For example, in passenger car tyres the performance factors such as wet grip and rolling resistance (contributing to total fuel efficiency) are intimately linked to the viscoelastic properties of the tyre tread material. Some of these modifications can be understood in terms of the structural dynamics of dissipative yielding and stress softening of fractal filler structures under increasing dynamic loadings; but even at small, linear viscoelastic strains where such yielding does not take place, the modification of the viscoelastic spectrum cannot be fully explained in an analytical sense by hydrodynamic, rigid volume reinforcement concepts alone [1–3].

To address this problem, a number of authors have proposed and/or demonstrated that the local segmental

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dynamics of certain rubber polymers in the vicinity of a range of filler particles can be substantially altered versus the corresponding bulk polymer material [4–6]. Furthermore gradients of chain mobility proceeding from the polymer in direct contact with the filler surface to bulk behaviour have been reported as well as 'bridges' of glassy polymer between filler aggregates where confinement of the polymeric macromolecules is particularly extreme. Some authors have proposed a theoretical model for these effects based around the percolation of small, localised density fluctuations within the polymer phase [7]. It has also been proposed that the existence of a broadened glass transition can account for a range of phenomena associated with particulate reinforcement such as the Payne and Mullins effects [8]. Conversely there are a large number of studies that report no significant effect of the presence of filler on the local segmental dynamics of the polymer and the bulk glass transition. This disagreement within the literature (up to 2008) has been highlighted by the topical review of Robertson and Roland [9]. While a considerable amount of work has been published on the behaviour of thin polymer films [10,11] with some reports of equivalence between confinement effects in thin films and bulk nanocomposite properties [12], no universal conclusions have yet been reached. Table 1 highlights the findings of a brief, and in no way exhaustive, selection of historical and more contemporary investigations which examined such glass transition effects specifically for the case of filled elastomers.

Some of the studies described in Table 1 were performed on conventional, commercial filled elastomers, others were performed on elastomers filled with esoteric, non-conventional fillers and a number were conducted on model nanocomposite systems comprising nanoscale particulates of near perfect dispersion within an elastomer matrix. Such a wide variety of sample types may have led to a range of different conclusions and interpretations as to the effect of filler particles on the polymer glass transition.

This work evaluates a series of silica and carbon black-filled natural rubbers using Differential Scanning Calorimetry (DSC), Broadband Dielectric Spectroscopy (BDS) and Dynamic Mechanical Analysis (DMA) techniques in an attempt to determine if the segmental dynamics and glass transition of the polymer in proximity to the filler surface are significantly modified and to what extent this can be correlated with the viscoelastic properties of the filled elastomers.

2. Experimental section

2.1. Specimen preparation

2.1.1. Carbon black-filled specimens

The preparation and detailed characterisation of the carbon black-filled samples has been reported in a separate publication [41]. A series of commercial carbon blacks were used, along with 'graphitised', thermally deactivated counterparts which display a significantly reduced interaction with the polymer phase. Key characteristics of the fillers are reproduced in Table 2 from Tunnicliffe et al. [41]. The Natural Rubber (NR) used was SMR CV60 grade obtained from the Tun Abdul Razak Research Centre (TARRC), Hertfordshire, UK. All carbon blacks were compounded with NR in a Banbury internal mixer. Mass loadings of fillers were adjusted to maintain equal volume fractions of 0.20; equivalent to 50 phr (parts per hundred rubber) of unmodified carbon black. Subsequently 2 phr of dicumyl peroxide (Fisher Scientific) was added on a laboratory 2-roll-mill. Samples were cured as 2 mm thick flat sheets using a compression mould and hot-press. The curing temperature was 150 °C and the curing time was 100 min – which was determined via an Alpha Technologies MD2000 rheometer to be the time required for near total decomposition and reaction of the peroxide. Subsequent analyses were performed with samples cut from the cured sheets.

2.1.2. Precipitated silica-filled specimens

Commercial precipitated silicas were investigated, together with tri-ethoxyvinyl silane (TEVS) modified counterparts. Conventional (CS) and highly dispersible (HDS) grades of silica were used. For the conventional silica the surface modification was pre-reacted with the silica by the supplier. For the highly dispersible silica the surface modification was performed *in situ* during compounding. All silicas were compounded with NR on a laboratory 2-roll-mill with the exception of the HDS with TEVS surface modification. This was prepared in a Banbury internal mixer in order for the mix to reach a sufficiently high temperature to promote reaction of TEVS with the silica surface. TEVS (Fisher Scientific) was added to the HDS on a nitrogen surface area basis to obtain a theoretically equivalent fractional surface coverage with the TEVS-pretreated CS. Sample mass loadings were adjusted to maintain equivalent volume fractions with the carbon black-loaded specimens (0.20). Further specimen processing was identical to that detailed for carbon black-filled specimens. Key characteristics of the fillers are reproduced in Table 2.

2.1.3. Specimens for BDS

For BDS, samples having a thickness of roughly 0.7 mm were made by the same compression moulding method. Samples were cut into 25 mm × 25 mm × 0.7 mm square sheets then gold electrodes were coated on both sides of each specimen by evaporation deposition. The diameter of the concentric gold circle electrodes was 22 mm. Due to the carbon black's inherent conductivity which, when the filler is loaded at significant volumes both below and above the electrical percolation threshold, can mask the polymer chain segmental relaxation process, the carbon black series of samples were not extensively investigated using BDS. However as an example, one carbon black sample (N330) was prepared at a volume fraction (0.05) well below the filler electrical percolation threshold [41] and subjected to BDS testing.

2.2. Experimental techniques

2.2.1. Differential scanning calorimetry

Calorimetry measurements were made using a Perkin Elmer Pyris Diamond DSC. Small samples (~10 mg) were