32.1 INTRODUCTION

The elastomers which cannot undergo strain-induced crystallization are generally reinforced with permanent reinforcing fillers [1–5]. The incorporation of fillers into polymers has the advantage of increased tensile strength, tear strength, abrasion resistance, resilience, and extensibility. However, the incorporation of fillers into a polymer has several disadvantages including increases in hysteresis and thus heat build-up resulting permanent deformation [1–5]. Two of the most important examples for the use of reinforcing fillers are the incorporation of carbon black fillers into natural rubber and to some other elastomers [6–8] and the incorporation of silica fillers into siloxane polymers [5,9]. Other polymers that have been reinforced using fillers include acrylates [10–13], polyamides [13], polyimides [15], polybenzoxazoles [16,17], and polybenzothiazoles [16,17]. Fillers such as titania, zirconia, mixed fillers of silica–titania and silica–zirconia, clays, metallic particles, and even glassy polymers have been used to achieve reinforcement.

The focus of this review is the properties of polymers reinforced with silica, however, the synthetic approaches of incorporating silica into polymers will also be briefly discussed.

32.2 IN SITU GENERATION OF SILICA

Experimental evidences indicate that the extent of the reinforcement depends strongly on the particle size. The maximum reinforcement is obtained for particles with diameters ranging from 10 to 100 nm. Although polymers filled with such nanoscaled silica fillers, i.e., polymer–silica nano-composites can be prepared by a variety of approaches, the majority of such composites are prepared through the sol–gel technique. Sol–gel reaction of a silicon alkoxide is a method for preparing inorganic silicon oxides under mild conditions [18]. It involves simultaneous hydrolysis and condensation of silicon alkoxide to form a three-dimensional silica network.

The sol–gel reaction has been used to in situ precipitate very small, well-dispersed silica particles into a polymeric material [19,20]. Silica particles thus produced give good reinforcement to a variety of elastomers. This technique avoids the difficult, time-consuming and energy extensive process of blending agglomerated filler into high molecular-weight polymers, especially when this is applied to elastomers. Insitu precipitation of silica using sol–gel technique can be done after, during or before crosslinking [20]. In situ filled elastomer is then extracted with a good solvent to achieve reinforcement. Various polymeric phases such as elastomers, glassy polymers, semicrystalline polymers and high-temperature polymers have been reinforced with silica in situ generated by the sol–gel technique [21,22].

Among elastomers, poly(dimethyl siloxane) (PDMS) has been the most extensively studied polymer with in situ generated filler. PDMS has frequently been chosen since it is compatible with silica or any other organometallic material used to generate ceramic phases. In addition, being a low-strength material, PDMS requires a considerable reinforcement from fillers before it is useful in many industrial applications [5,6]. A large number of other elastomeric phases including poly(phenyl methyl siloxane) [20,21], polybutadiene [21,23], and polyisobutylene [21,24] have been reinforced with silica using the sol–gel approach. Examples of glassy polymers [21] reinforced with in situ
generated silica include polyacrylates [12], poly(vinyl acetate) [25–27], and polyanilines [28]. Semicrystalline phases treated by the sol–gel technique include poly(tetramethylene oxide) [29,30], poly(ethylene oxide) [31,32], and poly(vinyl alcohol) [21,22]. Although it is difficult to treat high-temperature polymers in the usual sol–gel technique, few studies on aromatic polyamides [33,34], polyimides [35–40], polybenzobisoxazoles [16,17], and polybenzobisthiazoles [16,17] have been reported. High-temperature, high-performance polymers are generally unreactive which cause poor bonding between the polymeric and ceramic phases. This problem can be minimized by functionalizing the polymer or by adding a bonding agent [16,17,21,41].

32.3 CHARACTERIZATION TECHNIQUES

Polymer–silica nanocomposites thus prepared are characterized by electron microscopy, scattering techniques, nuclear magnetic resonance spectroscopy, etc. to determine the structural features. In addition, properties such as mechanical, thermal, optical, and other important physical properties are generally determined.

32.3.1 Structural Features

Electron Microscopy

Both transmission electron microscopy (TEM) and scanning electron microscopy (SEM) have been used to determine structural features of various polymer–silica systems. Electron microscopic techniques generally provide information on the nature of the filler, average particle size, or the distribution of particle sizes, smoothness of the interfaces, and the degree of agglomeration of particles.

Transmission electron micrographs obtained for silica-filled PDMS elastomers in base (ethyl amine) catalyzed hydrolysis of tetraethoxysilane (TEOS) and acid (acetic) catalyzed hydrolysis of TEOS are given in Figs. 32.1 and 32.2, respectively [2,3]. Figure 32.1 shows the particles in this silica-filled PDMS network have an average diameter of approximately 80 Å which is a very much desirable size with regard to reinforcement. Figure 32.1 also indicates that the filler particles have a relatively narrow size distribution, very little agglomeration, and well-defined surfaces. On the other hand, acidic catalysts yield poorly defined, agglomerated particles (Fig. 32.2) [2,3].

Electron microscopic results on networks filled in situ by the sol–gel approach have shown that the filler particles typically have a narrow distribution of sizes, with most diameters in the range 200–250 Å. TEM studies on the distribution of silica in situ generated within PDMS have shown that well-distributed particles can be obtained by using basic catalysts, thin samples, and long hydrolysis times [42]. TEM was also used for characterizing PDMS networks filled with silica–titania and silica–zirconia mixed oxides [48–50]. The distributions of particle sizes in such systems were relatively narrow with average particle diameter approximately 200–250 Å which increased to 300–350 Å when the molecular weight of the PDMS chains increase from 18,000 g/mol to 26,000 g/mol presumably due to the confining effect of the network pores. The silica–zirconia mixed oxide fillers were found to have particle sizes and distributions very similar to those of the silica–titania ones [48–50].

TEM studies performed on silica filled poly(tetramethylene oxide) by the sol–gel process showed an increase in the...