Investigation of the rubber elasticity and properties of polyurethane elastomers with different silicon carbide contents

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Abstract. Silicon carbide (SiC) powder was added to a polyurethane elastomer (PUR) to produce the composites. PUR was synthesized by mixing polyether polyol (PETP, Mₐ = 6000 g/mol) and 4,4′diphenylmethane diisocyanate. The stress-strain curves were carried out to estimate the effect of SiC on rubber elastic behaviour of PUR composites. As SiC content increases, the rubber elasticity region is noticeably decreased which can clearly be seen in the stress-strain curve, this could be attributed to the distribution of the SiC particles in the PUR matrix which prevents the cross-linking chain mobility of PUR and therefore affects the deformation while stretching. Furthermore, the decrease in the elongation at break is also correlated to the SiC content which hindrance the molecular mobility of the PUR chain. Shore A and D hardness increase by increasing SiC content up to 88 Shore A and 37 Shore D at 30 wt.% SiC. This is mainly due to the addition of SiC particles which act as active fillers in PUR matrix. The tensile strength and Young’s modulus are slightly increased when SiC content was increased. These observations support that SiC particles act as reinforcement which is active fillers and affect the stiffness in the elastic deformation of PUR.

1. Introduction

The research growth in the area of composite materials is becoming more attractive and widely spreading field of material science [1-4]. Silicon carbide (SiC) is a ceramic material that has unique physical properties such as good thermal conductivity, high-temperature stability, notable wear resistance, superior chemical resistance, good electron mobility and outstanding mechanical properties [5]. Several types of research have been done regarding the addition of SiC nanowire to the polymer matrix to enhance the thermal conductivity of the composite materials [6-7]. The different weight ratios of SiC particles in polyester composites were investigated and correlated to the mechanical properties such as tensile, flexural, compressive and impact strength [8]. It is similar to the effect of the addition of SiC on the mechanical properties of polyamide (PA6). Mechanical properties, such as tensile strength, impact strength and modulus of the PA6 composites were found to be significantly higher than the pure PA6 [9]. An increase in thermal stability of the polyurethane composites was observed with the addition of the silicon carbide nanoparticles. Moreover, tensile strength was observed to increase dramatically with the increase of the particle loading [10].

Polyurethane elastomers (PUR) have several advantages and widely used in industry due to the superior properties such as high impact strength, good elasticity, high elongation etc. Moreover, polyurethane is a special polymer that consists of hard and soft segments. The properties can be easily
enhanced by changing the molecular chain structure of the soft and hard segments [11]. Although many research works in polyurethane and high thermal conductive filler composites have been conducted, for example, polyurethane reinforced carbon black [12], boron nitride [13-14], and silicon carbide [10]. Only few focus on the reinforcement of the polyurethane matrix with silicon carbide to enhance the thermal conductivity. Therefore, the aim of this study is developing polyurethane elastomer composites for high thermal conductivity applications. This work investigates the effect of the addition of submicron silicon carbide to the PUR matrix on the properties of the produced composite materials.

2. Experimental

2.1. Materials
Silicon carbide powder was purchased from Minerals Water, United Kingdom. The particle sizes are 25 µm. The main raw materials (polyether polyol and isocyanate) were supplied by BorsodChem Zrt. (Hungary). Caradol MC28-02 is used as a polyether polyol. ONGRONAT XP1117 is used as an isocyanate part of this synthesis. Moreover, polypropylene glycol (PPG-400), ethylene glycol, amine catalyst and moisture scavenger were also used for this work.

2.2. Methods
Polyurethane elastomers were synthesized and prepared by using an appropriate amount of the raw materials as shown in table 1. Firstly, several polyol blends were prepared by mixing different amount of the polyether polyol (Caradol), polypropylene glycol (PPG), amine catalyst and moisture scavenger. After that, SiC (10-30 phr) powder was mixed in polyol blend via the homogenization machine for 10 minutes. The dried mixture was mixed with isocyanate part (MDI) by homogenization machine for 8 to 15 seconds and suddenly poured into the warm mould at 50°C for 15 to 30 minutes.

2.3. Testing and characterization
Rubber elasticity and other properties of polyurethane elastomers and its composites were tested according to ISO 527 using Instron Universal Testing Machine. The cross-head speed of 100 mm/min was operated at the room temperature. Both Shore hardness (A and D) were tested according to ISO 868. Viscoelastic properties were investigated by a Dynamic Mechanical Thermal Analyzer DMA 8000 (PerkinElmer). Storage modulus and tan delta were analysed from -80 to 150°C with bending mode at 1 Hz and a heating rate of 2°C/min. Furthermore, thermal conductivity was measured using a C-THERM thermal conductivity analyser (TCi) at room temperature and morphological properties were studied using Scanning Electron Microscopy technique (SEM; ZEISS EVO-MA10).

3. Results and discussion

3.1 Tensile properties
Stress-strain curves, tensile properties of polyurethane elastomers and SiC composites were shown in figure 1 and 2, respectively. The curve can be clearly shown the slope at the beginning tends to increase with increasing SiC content, which confirms that Young’s modulus was improved. This is good indication that SiC particles act as reinforcement fillers and affect the stiffness in the elastic deformation region. On the other hand, the deformation before break-up of the composites decreased. This can be clue that SiC particles obstruct the cross-linked chain mobility of polyurethane elastomers.

For the tensile strength, it slightly increases from 7 to 9 MPa when SiC content was increased. The elongation at break value trends to decrease from 185 to 131%. This result could be assigned to the poor adhesion between SiC fillers and PUR matrix and because of their inherent incompatibility, the elongation at break is decreased [15]. In contrast, Young’s modulus was enhanced with increasing SiC content by 1.7 times from 18 to 31 MPa as shown in figure 2(b). This suggested that dispersion and content of SiC affect the stiffness in the elastic deformation of the PUR matrix.
Table 1. Components of polyurethane elastomers

| Component                                      | Weight fraction (phr) |
|------------------------------------------------|-----------------------|
| Polyether polyol (Caradol MC28-02)             | 100                   |
| Polypropylene glycol (PPG-400)                 | 5                     |
| Amine catalyst (Dabco 33-LV)                   | 0.6                   |
| Monoethylene glycol                            | 10                    |
| Moisture scavenger (Finmasorb 430 PR)         | 5                     |
| Silicon carbide (SiC)                          | 0-30                  |
| 4,4’-diphenylmethane diisocyanate (MDI: ONGRONAT XP1117) | 22-31                 |

3.2 Hardness and density
Shore A and D hardness values of PUR and SiC composites show slightly increase with increasing SiC content. Shore A hardness increases from 81 to 88 while Shore D hardness increases from 26 to 37 as shown in figure 3(a). This result can confirm that the SiC content and dispersion are highly influenced stiffness of PUR composites. Furthermore, the density results show a correlation between tensile strength, Young’s modulus and Shore hardness. It increased with increasing SiC content from 1.137 to 1.369 g/cm$^3$ as exhibited in figure 3(b).

3.3 Dynamic mechanical analysis (DMA)
DMA thermogram shows the storage modulus ($E’$) of PUR with different SiC contents from 0 to 30 wt.% as revealed in figure 4. Results show high storage modulus at the beginning (higher than $1\times10^9$ Pa) and it was increased with the addition of SiC fillers. This can be an indication that SiC acts as reinforcement fillers in PUR matrix and may be due to the good dispersion of SiC particles as mentioned in the literature [16].

![Figure 1. Stress-strain curve of polyurethane elastomers with different SiC content](image-url)
Figure 2. Tensile strength, elongation at break (a) and Young’s modulus (b) of polyurethane elastomer with different SiC content

Figure 3. Shore A hardness, Shore D hardness (a) and density (b) of polyurethane elastomer with different SiC content

For tan delta results, the graph at lower temperature can clearly reveal a sharp peak and the tip of this peak is around -46°C, it indicates the glass transition temperature of soft segment (T_{g,SS}) of PUR structure while the glass transition temperature of hard segment (T_{g,HS}) show a broader peak which is difficult to determine T_{g,HS}. With the addition of SiC fillers, T_{g,SS} did not change while T_{g,HS} decreased from -12 to -5°C with increasing SiC content as shown in figure 4. In the case of T_{g,SS}, increasing the amount of SiC did not influence the chain mobility of polyurethane elastomers while the shift of T_{g,SS} when reinforced by dispersion of inorganic fillers indicates the chain mobility [17]. For T_{g,HS}, decreasing of the glass transition temperature may be due to decreasing of cross-linking level in PUR structure [16]. The other reasons might be due to the fact that the addition of SiC fillers leads to decrease the hard segment chain length, hard segment crystallinity and phase separation [18]. Moreover, amplitude of tan delta peak tends to decrease with increasing SiC content, which confirmed in some research [19]. This can ensure that SiC content and its dispersion can highly influence the polyol segment motion in PUR structure and indicate the greatly restricted motion of polyurethane chains resulting from the crosslinking function of the filler for the isocyanate-terminated polyurethane chains [18].
3.4 Thermal conductivity
Thermal conductivity value trends to increase from 0.253 to 0.521 W/mK with increasing content of SiC from 0 to 30 wt.%. The thermal conductivity was enhanced by 2 times, as shown in figure 5. This result may be due to the high thermal conductivity of SiC particle and evenly dispersion of SiC particles in the PUR matrix. The other reason could be the improvement of the phonons propagation by SiC particles through a boundary which separates one phase from another [20].

3.5 Morphology
Scanning electron microscopy (SEM) was used to investigate the morphology of polyurethane elastomers and their composites. SEM image exhibit good mixing of the soft and hard segment as present in figure 6(a), the surface of the pure PUR showed a smooth surface with some contaminants. PUR with SiC SEM image clearly revealed the presence of two phases as shown in figure 6(b) and (c). SiC particles are evenly dispersed in PUR matrix. It can be seen that particles were buried inside PUR. Furthermore, flake-like shape and micro-sized of SiC particles were revealed and it can be observed that coarse particles have fragmented to smaller particles as shown in the dash circle line of figure 6(b) and 6(c).
4. Conclusion
In conclusion, the addition of the silicon carbide can improve Young’s modulus in the elastic deformation region of PUR composites. Moreover, increasing SiC content can enhance the tensile strength, Shore A and D hardness and storage modulus of PUR composites because SiC particles acting as active fillers in PUR matrix. This effect was not expected in this study. In contrast, the elongation at break tends to decrease when SiC content was increased. This can indicate that SiC particles and its dispersion made the PUR matrix lose its elastic deformation due to their inherent incompatibility between SiC particles and PUR matrix. $T_{g,SS}$ did not change while $T_{g,HS}$ decreased with addition of the SiC fillers. These results indicated that SiC fillers and its content did not or hardly affect the chain mobility of PUR, therefore, $T_{g,SS}$ did not shift. Decreasing of $T_{g,HS}$ with the addition of the SiC indicate decreasing the cross-linking, hard segment chain length and phase separation of PUR structure. The amplitude of tan delta peak was decreased when SiC content was increased this is due to the restricted motion of polyurethane chains which affects the polyol segment motion. Furthermore, thermal conductivity was improved by 2 times due to the even dispersion of the SiC fillers in PUR matrix, which correlated to morphological properties.

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