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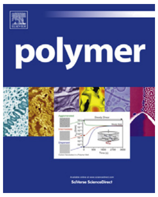

Green silicone elastomer obtained from a counterintuitively stable mixture of glycerol and PDMS

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ABSTRACT

A green and cheap silicone-based elastomer has been developed. Through the simple mixing-in of biodiesel-originating glycerol into commercially available polydimethylsiloxane (PDMS) pre-polymer, a glycerol-in-PDMS emulsion was produced. This counterintuitively stable mixture became a basis for obtaining elastomeric composites with uniformly distributed glycerol droplets. Various compositions, containing from 0 to 140 parts of glycerol per 100 parts of PDMS by weight, were prepared and investigated in terms of ATR-FTIR, broadband dielectric spectroscopy, mechanical properties as well as optical and scanning electron microscopy. The materials were proven additionally to exhibit a strong affinity to water, which was investigated by simple water absorption tests. Incorporating glycerol into PDMS decreased the Young's modulus of the composites yet the ultimate strain of the elastomer was not compromised, even in the presence of very high loadings. The conducted experiments highlight the great potential of this new type of elastomer and reveal some possible applications.

1. Introduction

Non-toxic, energy saving, biodegradable, made from recycled materials or renewable resources, made from industrial or agro-forestry residues – the qualification list for a polymer to be regarded as "green" is very long. Thus, fulfilling more than one of them generally leads to multiple issues in material preparation procedures, and it usually also compromises the material's ultimate properties [1]. Research on eco-friendly plastics has become one of the main targets of modern industry [2–5], and the prospect of an oil shortage motivates the material industry to look into innovative sources. Ideal alternatives to traditionally synthesised monomers seem to be substrates of natural origin; therefore, extensive investigations into the usefulness of bio-based monomers, as well as natural fillers (e.g. fibres), have been conducted successfully [6–10]. Nonetheless, not many reports have been presented on green elastomers. The significant extensibility of these materials is a very unique property that requires an uncompromised balance of physical and chemical properties in their structure, and so the task of preparing commercially attractive elastomers is a highly complicated procedure. Nevertheless studies exist representing successful attempts at using bio-based substrates and incorporating them into elastomers. An interesting example is the work of Brook et al., who employed softwood lignin, acting as a crosslinker, and at the same time as a reinforcing agent in silicone elastomers [11]. Furthermore, in other approaches the biodegradability of various elastomers has extensively been investigated and finally improved [12–15]. This indicates that there is a need for developing green elastomers, although the preparation procedures still require further optimisation.

It is common knowledge that glycerol, as a residue of biodiesel production, offers great potential in the preparation of a new wave of green polymers. Considering the fact that biodiesel production in European Union increased fourfold between 2004 and 2008, and that 100 kg of glycerol is obtained from 1000 kg of biodiesel, it is believed that more attention should be afforded to research on glycerol-based polymers [16]. Thus, so far, multiple research groups have investigated the usefulness of this compound in organic

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chemistry and material science [17,18]. One common example of applying glycerol in polymer science is using it as one of the monomers in polymer synthesis [13,19,20]. Introducing glycerol into polymers as one of the substrates brings these materials closer to the definition of “green” polymers, although the amounts of glycerol used in such cases are usually insignificant compared to other reactants, whilst in addition the resulting polymers become significantly more expensive.

Adding solid fillers to elastomeric or non-elastomeric polymers is usually intended to improve material properties or decrease the overall price of the product. In either case, adding fillers significantly influences material features over time, i.e. product reliability is reduced [21]. For example, in the case of polydimethylsiloxane, incorporating silica particles is a vital process that allows for obtaining highly stretchable materials with good ultimate properties. On the other hand, incorporating rather inexpensive fillers, such as wood-dust, is a common procedure for decreasing a product's price [22]. In our approach we present an innovative way of identifying the introduction of fillers into elastomers. We investigated the possibility of using glycerol as a liquid filler of a polar nature incorporated into a commercially available, highly non-polar, silicone elastomer. We found that incorporating glycerol into PDMS does not compromise the ultimate strain of the material, thereby making it much cheaper compared to non-glycerol PDMS. Samples with different amounts of glycerol were prepared and extensively investigated in terms of their morphology and mechanical properties. The conducted experiments revealed and finally proved the great potential of this new type of green and cheap elastomer.

2. Experimental

2.1. Materials

A two-component silica-filled Sylgard 184 silicone kit (S184) was purchased from Dow Corning US. Glycerol (food grade), as a byproduct of biodiesel production, was provided by Emmelev A/S Denmark and was used as received, avoiding excessively long contact with the air.

2.2. Methods

A dual asymmetric centrifuge SpeedMixer DAC 150 FVZ-K was used for mixing all of the compounds. A Leica DM LB optical microscope was applied for investigating glycerol in silicone emulsion morphology. Viscosities of the investigated pre-polymer formulations were determined with the help of an ARES AR2000ex rheometer from TA Instruments using a conical concentric cylinder geometry at a steady state flow measurement. Data points used for comparison of viscosities were obtained from shear rate of 0.1 1/s. A FEI Inspect S scanning electron microscope was used to obtain images of cured specimens' cross-sections. Samples were gold-sputtered prior to testing, in order to obtain higher quality images. ATR-FTIR spectra of composite cross-sections were obtained with the help of a Nicolet iS50 FT-IR spectrometer, while tensile tests were performed on an Instron 4301 universal tester at room temperature at a strain rate of 500 mm/min – as stipulated by ASTM D412-C standards. Sample conductivity was investigated with a Novocontrol broadband dielectric spectrometer. Disc samples, 20 mm in diameter and 1 mm thick, were tested in frequency ranges between 10^6 and 10^{-1} Hz.

2.3. Sample preparation

The Sylgard 184 silicone kit was mixed in a 10:1 ratio by weight, as recommended by the manufacturer. Subsequently the desired amount of glycerol was added to PDMS and stirred with the help of the speed-mixer for 5 min at 3500 rpm, unless mentioned otherwise (3500 rpm is the maximum rotational speed of the device). No additional degassing of the formulations was necessary, due to the dual asymmetric method of mixing, which effectively pushes out entrapped air voids. After the mixing step, all compositions were cast onto a metal mould with a 1 mm spacer and cured at 80 °C for 1 h. Obtained films were then left at room temperature for at least two days, in order for eventual post-curing to take place. Samples for tensile tests were prepared according to ASTM D412-C standards. Mixed formulations were cast onto a PMMA plate with a 3 mm spacer. After curing, the samples were cut with a custom-made die.

The abbreviation ‘phr’, used to describe glycerol content in all compositions, corresponds to glycerol weight amount per hundred weight parts of silicone rubber. Sample names were formed using the pattern GX_S184, where G and X stand for glycerol and glycerol phr added to a PDMS prepolymer, respectively. Intuitively S184 corresponds to the applied PDMS system.

3. Results and discussion

3.1. Glycerol in PDMS emulsions and the morphology of cured samples

The morphology of glycerol in PDMS emulsions obtained by direct mixing the two virtually immiscible liquids was analysed with the help of optical microscopy. Proper mixing conditions were determined with a simple test, in which a composition of prepolymer and glycerol was mixed at different speeds and increasing mixing times. It was found that an increase in shear forces has a tremendous impact on glycerol droplet size (see Fig. 1), in that the higher the rotational speed, the more mono-dispersed emulsions are obtained. The maximum droplet diameter decreased from around 30 μm to around 3 μm for the same formulations mixed for 5 min at 1000 and 3500 rpm, respectively. Longer mixing times were proved to have a negligible impact on droplet size, though for each glycerol concentration a minimum mixing time that ensures obtaining an agglomeration-free emulsion is required. Therefore, most compositions were mixed for 5 min at 3500 rpm, which provided sufficient shear forces for obtaining reasonably mono-dispersed emulsions for a broad range of glycerol incorporated into PDMS. The images shown in Fig. 2 present various uncured compositions with increasing amounts of incorporated glycerol. Viscosities of the obtained emulsions are presented in Fig. 3. Produced mixtures were stable for extensive amounts of time. No change in droplet size was observed, even several hours after mixing.

Cross-sections of crosslinked composites were investigated through scanning electron microscopy. The images presented in Fig. 4 show the cross-sections of four samples with 10, 50, 90 and 130 phr of incorporated glycerol, respectively. As can be seen, when the amount of glycerol increases, droplet concentration becomes higher; however, the average droplet size remains almost uninfluenced. It was additionally observed that while increasing the glycerol/PDMS ratio of formulations, a threshold concentration is finally reached above which a droplet-like morphology is no longer present in the crosslinked material. Instead, a network with interconnected glycerol channels is formed. This phenomenon was additionally proved by testing the conductivity of the compositions. Broadband dielectric spectroscopy tests showed that the sample with 140 phr of glycerol exhibited slightly increased conductivity compared to formulations with lower glycerol concentrations (see Fig. 5). This is in agreement with our expectations, since it is