

Effect of Titanium Dioxide on Material Properties for Renewable Rapeseed and Sunflower Polyurethane

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Abstract

Polyurethanes (PUs) have been synthesised successfully from renewable resources namely as rapeseed and sunflower oil using 4,4'-methylene-bis-(phenylisocyanate) (MDI) as the cross-linking agent. The mechanical property of these materials was observed in the Dynamic Mechanical Thermal Analysis (DMTA) test. A high tan delta peak is essential for a good damping material. These PUs can be strongly influenced on the addition of small (2.5-10) percentages of titanium dioxide, TiO_2 , e.g. the damping was improved on adding TiO_2 . Upon UV-induced aging, two important changes occur as observed in mechanical damping, such as a decrease in the height of the tan delta peak and a shift of the temperature of the tan delta peak to higher values with increased irradiation time. The loss tan delta peaks for the rapeseed-based PU loaded with 2.5, 5, 7.5, 10% of TiO_2 were 0.58, 0.6, 0.68, and 0.71 respectively as compared with neat RSPU at only 0.43. These data show that the damping ability is enhanced through the introduction of TiO_2 into the polymer. By doping with TiO_2 , the mechanical or physical properties of these PUs can be altered systematically, such as to get progressive increases in its stiffness and damping property.

Keywords: Polyurethanes, 4,4'-methylene-bis-(phenylisocyanate), damping, titanium dioxide, rapeseed.

1. INTRODUCTION

Chemistry and engineering teams are now working to transform renewable raw materials into new chemicals, polymers, formulated products and composite materials, known as “Bio-Materials”. The sustainability of this industrial sector is dependent in the long term on a fundamental shift in the way in which resources are used, from non-renewable to renewable, from high levels of waste to high levels of reuse and recycling, and from products based on lowest first cost to those based on life cycle costs and full cost accounting, especially as applied to waste and emissions from the industrial processes that support construction activity [1].

When discussing bio-materials, it may seem elementary, but it is important to note that plants do not cause any negative effects to the ecosystem, they can grow in different climatic zones, they recycle the carbon dioxide for the atmosphere of our Earth, and many works to improve soil fertility [2]. Therefore, it is necessary to shift our usage from petroleum-based product to renewable and recyclable materials since renewable resources generally do not contain environmentally damaging substances and reduce our landfill requirements.

Since about 1990, genetically modified oils have been developed using either mutation/selection breeding or the tools of biotechnology, and represent some of the most significant new products developed for the oils and fats industry [3]. The main constituent of these oils is saturated and unsaturated fatty acids that are unique to the plant in which they have been developed. Modern technology can produce more well defined and pure oils, and fatty acid contents in the vegetable oil can be altered with modern crop development techniques.

1.1 Polyurethanes from Renewable Resources

The development of novel feedstocks for polyurethanes derived from renewable materials has become important because the use of polyurethane polymers is increasing at a rate of 1 million tonnes a year [4]. This level is unsustainable in the long term without the development of alternative sources. Oils from vegetable crops can be manipulated chemically

to produce a variety of polymeric materials, including polyurethane products. The reaction of organic isocyanate with compounds containing OH (hydroxyl) groups is capable of wide application in polymer formation [5]. Thus the urethane linkage, $-(NHCOO)-$ can be produced by reacting compounds containing active hydrogen atoms with isocyanate, where polymer formation can take place if the reagents are di- or polyfunctional, according to the following reaction:

$RNCO + ROH \rightarrow RNHCOO$ isocyanate hydroxyl group / (diols) urethane

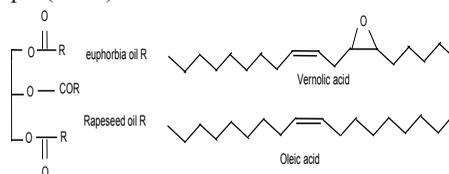


Figure 1.2: Renewable vegetable oils that are rich in fatty acids

Although the unsaturated vegetable oils such as rapeseed or euphorbia do not contain the necessary hydroxyl group as a chemical functionality for making polyurethane polymers, they both contain oleic acid and vernolic acid respectively (refer to Figure 1.2). These fatty acids can be manipulated by the introduction of Venturello’s catalyst and hydrogen peroxide to give epoxides, followed by ring opening to form polyols. Thus, hydroxylated feedstocks are available for use in the polyurethane and polyester sector. Moreover, the epoxides can be used for making epoxy resins.

1.2 Modification of Polymers using Fillers

Fillers, either particulate or of fibrous nature, as glass, metal oxides, natural fibres and metals, have been added to thermoplastics and thermosets for decades to form polymer composites. Fillers are used in polymers for a variety of reasons: cost reduction, improved processing, for example in curing with a cross-linking agent such as in sulphur vulcanization, density control, optical effects, thermal conductivity, control of thermal expansion, electrical properties, magnetic properties, flame retardancy and improved mechanical properties, such as hardness and tear resistance and many more reasons.

The term ‘functional filler’ is often used to describe materials that do more than provide

cost reduction. Examples of functional fillers include carbon black and precipitated silica reinforcements in tyre treads, the role of stabilisers to reduce in-process degradative effects, and many more miscellaneous additives for polymers such as blowing agents, impact modifiers, lubricants or antimicrobials. Increased polymer consumption over the past twenty years has not only stimulated developments in manufacturing plant, but has also led to a parallel growth in the usage of a large variety of liquid and solid modifiers, including fillers and reinforcements [5].

Fillers may be classified broadly as organic or inorganic substances, and further subdivided according to chemical family. In a recent review, Wypych reported more than 70 types of particulates or flakes and more than 15 types of fibres of natural or synthetic origin that have been used or evaluated as fillers in thermoplastics and thermosets [6].

According to Xanthos M. [7], the classification of polymer additives is according to their primary function and a plethora of additional functions. The scheme adopted by Xanthos involves classification of fillers according to five primary functions such as modification of mechanical properties, enhancement of fire retardancy, modification of electrical and magnetic properties, modification of surface properties and enhancement of processibility.

From the point of view of this paper should be added TiO₂ as modification of mechanical property, surface property, or as an optical agent. TiO₂ has an important role as a (white) colourant in synthetic polymers such as poly (vinyl chloride) which is used as a building material (windows, doors, fascia boards) and polyethylene film (the familiar supermarket shopping bag material) [8].

2. METHODOLOGY

2.1 Preparation of Hydroxylated Rapeseed (RS) Monomer

2.1.1 Condensation method

Rapeseed oils were obtained from Tesco plc and were chemically manipulated at the laboratory scale using less than 1L of vegetable oil. The preparation of the hydroxylated monomer was divided into two stages, beginning with the preparation of catalyst (hydrogen peroxide/tungsten powder/phosphoric acid) to generate the epoxides from the unsaturated fatty compounds, while the second stage is the of acid-catalysed ring-opening of the epoxides to form polyols.

2.2 Preparation of Rapeseed Polyurethane (RS-PU)

2.2.1 Methods of preparing RS-PU films

Thin films of renewable RS-PU were prepared by adding the hydroxylated rapeseed monomer (1 gm; 0.2 gm equivalent weight with polyol) with an appropriate amount of 4,4'-methylene-bis-(phenylisocyanate(MDI). The mixture was mechanically stirred until a viscous compound resulted which was left to cure in an aluminium dish at room temperature for at least 12 hours until the disappearance of N=C=O groups as measured by IR spectroscopy. The thickness of each sample was determined by using a digital vernier calliper at three different places and the average value was calculated. Samples were prepared such that the thickness was normally about 200 μm .

2.2.2 Preparation and curing of RS-PU and composite test specimens

The composite test specimens were prepared by mixing 15 g (3 g equivalent) of polyol, different percentages of MDI (such as 0.3 and 0.5% equivalent weight of polyol) and different percentages of titanium dioxide (such as 2.5, 5.0, 7.5 and 10.0 % equivalent weight of polyol). RS-PU samples, both neat, and with filler were prepared. The latter used titanium dioxide in different percentages (1.5, 2.5, 5, 7.5 and 10 %) as filler.

A distinction has been made during the curing process between:

a. the curing time

The curing time is when the reactant mixture, having become sticky, was poured into the mould and left until the material became tack-free. At this point the mould was clamped and put into the oven at 55°C for about 5 minutes.

b. the post-curing time

The post curing time is that for heating at 55°C outside the mould when the sample was sandwiched between two aluminium plates, to give an even and permanent shape of the resulting sample.

c. the maturation time

This is the time during which any secondary chemical reactions go to completion and the PU

structure becomes established; this period was at least 2-3 hours at room temperature, until the disappearance of N=C=O groups as measured by IR spectroscopy.

2.2.3 Testing conditions Dynamic Mechanical Thermal Analysis (DMTA)

A Tritec 200 DMTA (Triton Technology) instrument was employed for dynamic evaluation of the renewable rapeseed polyurethane. DMTA determines the viscoelastic properties of polymers. It measures the modulus (stiffness) and the damping (energy dissipation) properties as a polymer deforms under periodic stress. The sample strain response lags behind the input stress wave with respect to time and the lag is known as the phase angle (δ). The ratio of the dynamic stress to the dynamic strain provides the complex modulus that includes both the storage modulus, (E') and the loss modulus (E''). The storage modulus refers to the ability of a material to store energy and is related to the stiffness of the material. The loss modulus represents the heat dissipated by the sample as a result of molecular motions and reflects the damping characteristics of the polymer. The maximum heat dissipation occurs at the temperature where E'' is at a maximum, indicating the T_g of the system [9]. Rectangular test pieces of polyurethane (~15 mm long, 10 mm wide, 2.3 to 2.4 mm thick) were tested in a standard air oven with a single cantilever mode using test frame L and clamp type C at a frequency of 0.5 Hz with a heating rate 5°C/min. In this system, a sinusoidal stress is applied to a vibrator unit using a sinusoidal current. The stress imposed upon the specimen is therefore directly related to the amount of current delivered to the vibrator. All the specimens were studied between 25° C and 150° C.

Irradiation Sources

The instrument used was a 'Q-Panel' accelerated Weatherometer. The device is a UV radiation tank with 8 fluorescent bulbs (300 W) selected at UVB wavelength are fitted inside the apparatus. The moisture bath can also be used to force harsher conditions but was not used in this work. Samples of RS-PU and composites were mounted onto the plates and placed on the sides of the instrument (Figure 2.2.3).



Figure 2.2.3: Q-Panel, accelerated Weatherometer mounted with film samples.

3. RESULT AND DISCUSSION

The curves of moduli (including storage modulus, E' and loss modulus, E'') vs temperature for RS-PU are shown in Figure 3.1. The moduli for the RS-PU and SF-PU have no obvious difference. Figure 3.2 is a representative plot of the temperature dependence of $\tan \delta$ with and without UV irradiation for the RS-PU samples. The distinct transition relaxation peaks are obvious from the graph. The T_g before exposure of 90.1 °C changed significantly to that of 110.7 °C after 3000 h of UV irradiation.

Chailan et al. [10,11] reported that two important changes in mechanical damping properties occur during UV weathering of an EPDM rubber, such as a decrease in the height of the $\tan \delta$ peak and a shift of the $\tan \delta$ peak to higher temperature after an induction period. In the present case, essentially the same changes were observed after 3000 hours of UV irradiation of the RS-PU.

Also after exposure, significant increase in the storage modulus at all temperatures as shown in Figure 3.3. Milena et al. [11] also reported an increase in storage modulus for EPDM rubber. This is due to hardening caused by photodegradation in the samples over the entire temperature range. The observed increase in storage modulus for the RS-PU sample after exposure could either be due to oil/volatile loss from the polymer or to increased cross-linking in the network structure.

After exposure, the more pronounced increase of the storage modulus and, therefore,

hardening effect was evident at room temperature onwards. This temperature range corresponds to the environmental conditions, which will be applicable for a particular automotive component-window seal section.

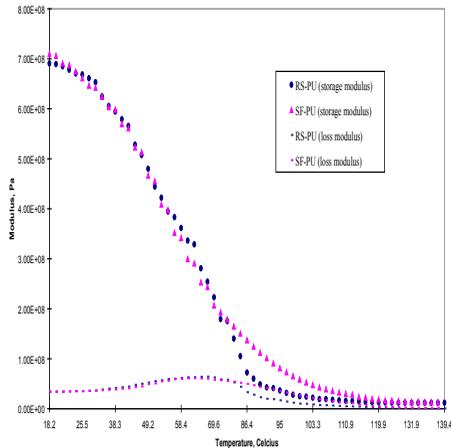


Figure 3.1: Value of storage modulus and loss modulus determined by DMTA for RS-PU and SF-PU.

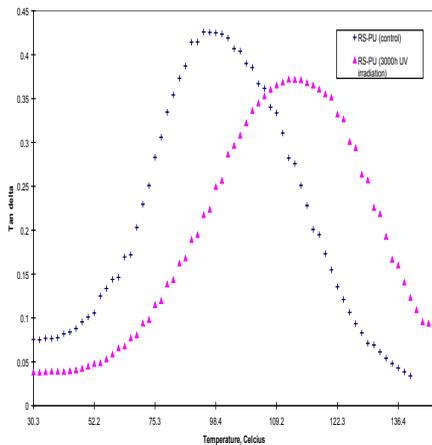


Figure 3.2 Value of tan delta determined by DMTA for RS-PU (unirradiated or control sample and irradiated to UV for 3000 hours)

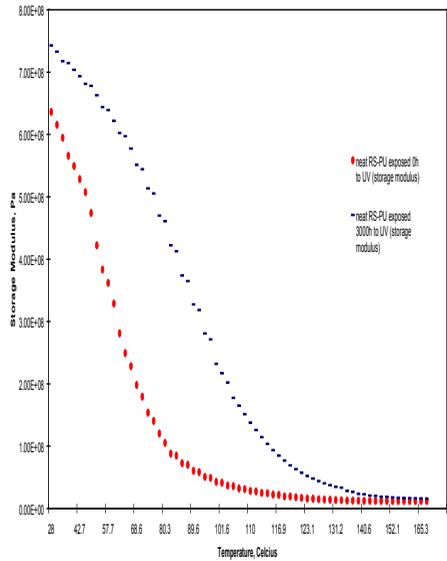


Figure 3.3. Values of storage modulus determined by DMTA for neat RS-PU (unirradiated or control sample) and sample UV- irradiated for 3000 hours.

3.1 Effect of addition of TiO₂ on DMTA for RS-PU properties

The progressive addition of TiO₂ has the effect of sharply increasing the value of tan δ , for both unexposed and exposed samples to UV-irradiation. Figure 3.4 shows the influence of TiO₂ loading and extensive UV-irradiation on RS-PU where the T_g values for all samples were shifted to higher temperature (5110°C) and decreased in value of tan δ (0.20.8) after UV irradiation, indicating that the damping properties of the samples are reduced on extensive UV-B irradiation (up to 3000 hours). From Figure 3.5 and 3.6, it is clear that there is an enhancement of E' (storage modulus) upon UV-irradiation, suggesting the production of higher stiffness [12] for RS-PU samples.

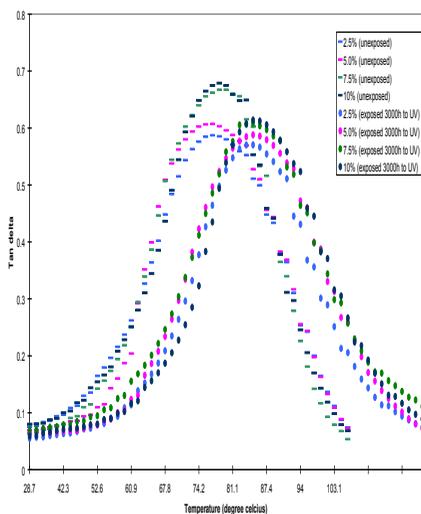


Figure 3.4. Influence of (i) TiO_2 loading and (ii) extensive UV-irradiation (for 3000 hours) on $\tan \delta$ value of RS-PU.

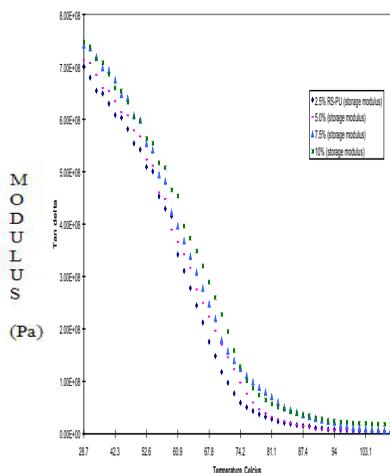


Figure 3.5. Influence of TiO_2 loading on RS-PU samples on E' (storage modulus) value for unirradiated samples.

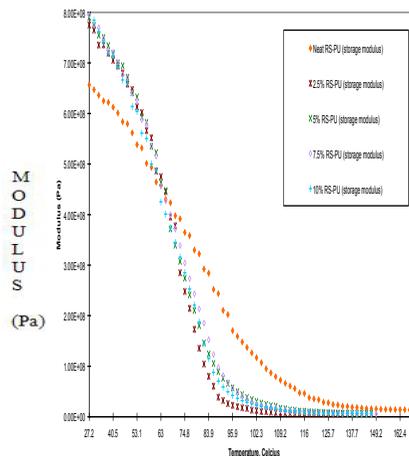


Figure 3.6. Influence of TiO_2 loading on RS-PU samples upon UV-irradiation. The E' (storage modulus) were increased in value with the extent of UV-irradiation up to 3000 hours.

3.2 Effect of addition of TiO_2 on DMTA for cross-link density for RS-PU

The cross-link density (ν_c) of a cross-linked polymer can be determined from the rubbery modulus by using Eqn. (3.1), based on the rubber elasticity [12-15]: $E' = 3 \nu_c RT$ (3.1) where E' is the storage modulus in the rubbery plateau above T_g (ca. $T_g \pm 40^\circ\text{C} = T$), R is the gas constant ($8.314 \text{ J K}^{-1}\text{mol}^{-1}$), and T is the temperature in Kelvin.

Sam ple	T_g ($^\circ$ C)	$(\tan$ $\delta)_{\max}$	E' , Pa)	ν_c (M/m^3) ($\times 10^3$)
0%	97.4	0.467 4	$1.27 \times$ 10^7	1.24
2.5%	78.6	0.587	$5.94 \times$ 10^6	0.607
5.0%	80.2	0.609 5	$5.56 \times$ 10^6	0.566
7.5%	82.3	0.678	$5.24 \times$ 10^6	0.553
10%	82.6	0.678 6	$5.24 \times$ 10^6	0.547

Unirradiated samples

0%	119.4	0.422 1	1.68 x 10 ⁷	1.557
2.5%	85.4	0.570	7.90 x 10 ⁶	0.747
5.0%	86.4	0.587	7.49 x 10 ⁶	0.747
7.5%	87.7	0.608 2	7.12 x 10 ⁶	0.712
10%	88.8	0.612 2	7.09 x 10 ⁶	0.709

UV Irradiated samples Table 3.1: Effect of UV irradiation on glass transition temperature, maximum of $\tan \delta$, and cross-link densities of RS-PU

Tan δ magnitudes of neat rapeseed based polyurethane after UV irradiation for 3000 hours show a decrease in the height of the peak maximum as the result of restricted chain mobility. Latere Dwan' Isa et al. [12] also reported that the values of $\tan \delta$ intensities of samples postcured for various time intervals show a decrease in the height of the peak maximum for the polyurethane prepared from soybean oil-derived polyols and polymeric diphenylmethane diisocyanate (pMDI). The restriction in molecular motion resulting from further cross-linking, that is higher v_g values, leads to augmentation of T_g and less dissipation energy throughout the thermoset, that is, lower values of $\tan \delta$ [12] (refer to Table 3.1). The T_g of the neat rapeseed-based polyurethane rises more than 20°C and the maximum enhancement of v_g is found to be 25.5% upon UV irradiation for 3000 hours.

Cross-linking influences the mechanical properties of polyurethanes [13,16-19]. Use of high-functional reactants, for example, polyol and diisocyanate, leads to a cross-linked network. Moreover, with an excess of diisocyanate ($\text{NCO/OH} > 1$), allophanate or biuret bonds form from excess diisocyanate-urethane that may cause chain branching and chemical crosslinking [6, 12]. Thus highly crosslinked polyurethanes useful for applications such as insulation materials or as automotive parts can be obtained [12].

4. CONCLUSION

This paper describes the results and conclusions for the study of the thermal and physical properties of RS-PU and SF-PU, doped and

undoped with TiO_2 . The result shows that doping has an effect on the thermal properties. The thermal resistance of both polyurethanes increases with the increasing level of TiO_2 . The DMTA results show an increase in T_g for on the addition of small (2.5-10) percentages of TiO_2 loading. Upon UV irradiation, the RS-PU samples show an increase in T_g for doped and undoped samples. The increase in values of the storage modulus indicates a hardening effect upon UV irradiation for RS-PU samples. By doping with TiO_2 , the physical properties of this polyurethanes (RS-PU and SF-PU) can be altered systematically, for example its stiffness, damping property and cross-link densities.

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