SYNTHESIS OF BARIUM SULFATE NANOPARTICLES USING DIFFERENT PLANT EXTRACTS WITH POLYCARBONATE EXTRACTED FROM ELECTRONIC WASTE TO MAKE POLYCARBONATE WITH ENHANCED PROPERTIES

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Abstract

More than one million tons of polycarbonates (PCs) from waste electrical and electronic equipment are consigned to landfills at an increasing rate of 3−5% per year. PCs that are disposed of in landfills or oceans can have a devastating impact on wildlife and the environment, as it contains harmful chemicals which will pollute the environment. (Weeden *et al.*, 2015) Furthermore, barium sulfate nanoparticles ($BaSO_4$) can be added into transparent polymers which include PC to enhance its properties like ultraviolet (UV) radiation stability, tensile strength, thermal conductivity and scratch resistance while maintaining the transparency of the PC (WIPO Patent No. WO2007039625A1, 2007). According to Chen *et al.* (2016), $BaSO_4$ nanoparticles can be synthesised to form nano-crystals using different types of plant extracts. PC can also be reinforced using $BaSO_4$ nanoparticles so as to improve its physical properties which may have practical applications and uses such as lenses or other materials that require long-lasting, durable polymers.

1. Introduction

PC has many uses such as in eyewear and plastic materials. PC demand has been increasing in volume in recent years, and are known to be made with of hazardous substances and improper waste treatment (Stenvall, 2013). The current annual global production of PC is around 3.45 metric tonnes in 2017, and it consumes about 24 million barrels of crude oil and 526 trillion British Thermal Units of energy. It also costs $2,50 to $5,00 per kilogram to manufacture, which is more expensive than other polymers (Weeden *et al.*, 2015). Some properties of PC include high durability, impact-resistance, higher transparency than most kinds of glass, UV light resistance and heat resistance. Thus, we will attempt to extract PC through more environmentally friendly processes.

$BaSO_4$ nanoparticles that are between 150 and 500 nanometres, both inclusive, can be added into transparent polymers like PC to enhance its properties in terms of ultraviolet (UV) radiation stability, while maintaining its transparency (WIPO Patent No. WO2007039625A1, 2007). According to Chen *et al.* (2016), barium sulfate nanoparticles can be synthesised to form nano-crystals using different types of fruit extracts, due to various biomolecules present such as proteins and carbohydrates which help in the synthesis.

PCs that are synthesised with $BaSO_4$ nanoparticles have been shown to possess improved qualities including scratch resistance and ultraviolet (UV) radiation stability, while maintaining excellent transparency (WIPO Patent No. WO2007039625A1, 2007). This makes $BaSO_4$ a highly suitable addition to PC to reinforce it, improving its strength and durability.

There have been experiments in the past by researchers to reinforce PC with $BaSO_4$ nanoparticles. However, the difference in our project is that we are experimenting with $BaSO_4$ that is synthesised from fruit extracts unlike reagent-grade, higher purity $BaSO_4$ used in past experiments. The PC we will be using will also be recycled from Waste Electronic and Electrical Equipment (WEEE) instead of newly-manufactured PC. By investigating with a different source of PC and $BaSO_4$, we will be able to compare the differences between the two yields of $BaSO_4$ in terms of its effects on the properties of the $BaSO_4$-synthesised PC and how $BaSO_4$ synthesised from fruit extracts may further enhance the properties of PC.

2. Objectives and hypotheses

Objectives

1. To extract PC from electronic waste using a cost effective and environmentally-friendly method.
2. To synthesise $BaSO_4$ nanoparticles by precipitation reaction using a suitable plant extract.
3. Investigate the enhancement in properties of PC reinforced with $BaSO_4$ nanoparticles.

Hypotheses

1. PC can be extracted from electronic waste using environmentally friendly methods
2. $BaSO_4$ nanoparticles can be synthesised using plant extracts.
3. $BaSO_4$ can be added to PC to create $BaSO_4$-reinforced PC with enhanced properties.

3. Methods and Materials

3.1 Materials

Compact Discs (CDs), Dichloromethane, CH_2Cl_2 (DCM), Acetone, $(CH_3)_2CO$ (ACE), 2M Hydrochloric acid, HCl, Fruit extracts (carrot, orange, lemon), Aqueous Barium Chloride ($BaCl_2$) and Aqueous Sodium Sulfate (Na_2SO_4)

3.2 Variables

Independent Variables	• Ratio of solvents (DCM:ACE) used to extract PC • Type of fruit extract used
Dependent Variables	• Quality of PC • The shape and size of $BaSO_4$ nanocrystals • Quality of $BaSO_4$-reinforced PC
Controlled Variables	• Mass & Volume of CDs • Amount of solvent used • Amount of each fruit extract used • The processes used to synthesise $BaSO_4$ and extract PC

3.3 Extraction of PC from electronic waste

CDs were cut into smaller pieces, blended and submerged in 2M Hydrochloric acid, HCl, for 24 hours to remove metal components in the CD, leaving the clear plastic behind. A 50ml mixture in separate ratios of 2:8, 3:7 and 4:6 consisting of Dichloromethane (DCM) and Acetone (ACE) were added to 5g of CDs to remove unwanted plastics such as Styrene acrylonitrile resin (SAN) and Bisphenol A (BPADP), leaving behind PC and Acrylonitrile butadiene styrene (ABS). Then, 20mL of DCM was added to retrieve the pure PC. The samples were then identified using Fourier Transform Infrared Spectroscopy (FTIR). The specific DCM:ACE ratio of 3:7 was selected as it is a strong to weak solvent ratio, as experimentation with other ratios like 2:8 and 4:6 have proved less effective, due to the difference in polarity between DCM and ACE with reference to that of PC.

The data observed from the PC extracted were the yield and purity of the PC, as well as the physical property of the PC, namely its tensile strength, which is one of the most important factors in judging the quality of polymers' properties.

Tensile strength can be obtained through the equation $s=P/a$, where s is the tensile strength in Psi, P is the breaking force in lbs, and a is the cross-sectional area in square inches. The breaking force was found through the use of a Kelvin material tester, while cross-sectional area was calculated by measuring the thickness and breadth of the films, and multiplying them together finding the area.

3.4 Synthesis of $BaSO_4$ Nanoparticles

Each fruit (Lemon, Orange, Carrot) was washed and juiced. The juiced was then centrifuged and the supernatant obtained. 10 mL of each fruit extract was then mixed with 20 mL of 0.05 mol/L $BaCl_2$. Each of the mixed solution was subsequently mixed with 20 mL of 0.05 mol/L Na_2SO_4 very slowly to form white precipitates of $BaSO_4$. The control experiment containing $BaSO_4$ was also performed with deionised water instead of fruit extracts and the above 4 reaction systems were stirred at room temperature for 24 hours.

The size and shape of $BaSO_4$ nanoparticles synthesised using varying fruit extracts were observed using Scanning Electron Microscopy (SEM). The size and shape of the nanoparticles were then deduced from the SEM images.

3.5 Synthesising PC with $BaSO_4$ nanoparticles

PC was first dissolved into DCM to form a solution. Then, $BaSO_4$ nanoparticles are added to the solution to form a suspension. After that, ACE, a non-solvent of PC, was then added to allow the PC to precipitate out, for an intimate mixture of PC and $BaSO_4$ nanoparticles to be formed. Finally, the whole mixture was filtered to obtain the solid.

The methods used to test the tensile strength of the PC reinforced with $BaSO_4$ nanoparticles were the same as that of the PC without $BaSO_4$ nanoparticles. The difference in tensile strength between PC reinforced with and without $BaSO_4$ nanoparticles were compared, so as to investigate the effectiveness of $BaSO_4$ as an additive to PC.

4. Results and Discussion

4.1 Characterisation of PC

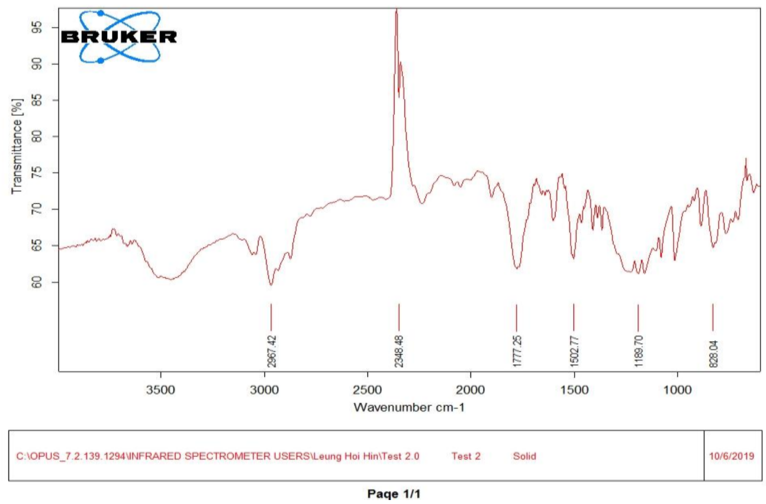

Fig. 1 (FTIR spectra of extracted PC)

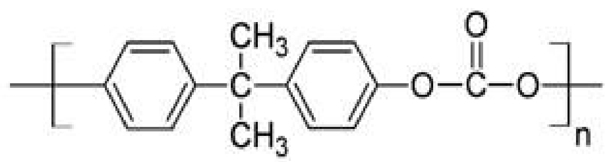

Fig. 2 (Chemical structure of PC)

Upon extraction, the PC was subjected to Fourier Transform Infrared Spectroscopy (FTIR). Based on the spectra obtained (Fig. 1), we can infer that the sample has high content of PC as the peaks mostly resemble that of online sources. Generally, the wavenumbers closely match the values online, and are found to be in accordance with the structure of PC (Fig. 2). Correspondingly, 2967 represents the C-H stretch, 1777 the C=O stretch, 1502 the Aromatic ring stretch, 1189 the C--O stretch and, 828, the Aromatic C-H out-of-plane bend. Thus, we can conclude that the extracted sample indeed contains the functional groups of polycarbonate. However, some impurities have also been found in the sample, such as the 2348 wavelength peak which represents carbon dioxide present that has been detected by the machine. Upon reviewing experimental processes, carbon dioxide in the spectra may have been introduced during the evaporation process, when air bubbles can cause the carbon dioxide to be trapped, contaminating the sample.

4.2 Tensile Strength

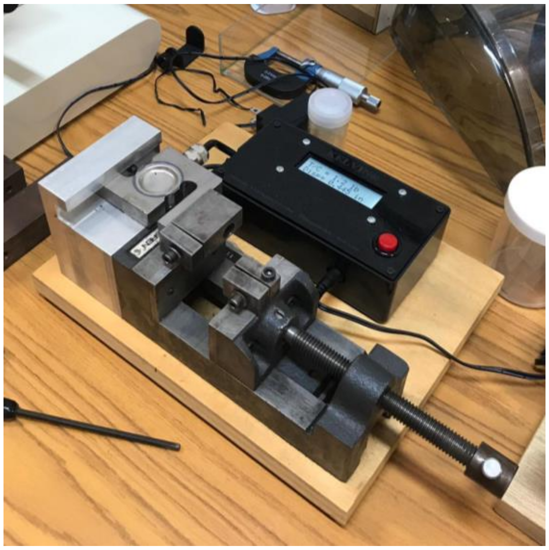

Fig. 3 (Kelvin Material Tester)

Types of PC samples (DCM:ACE ratios)	20:80	30:70	40:60
P/lbs	2.7	2.6	1.9
a/sq inches	0.00146	0.00132	0.00102
s/psi	1849	1969	1862

Fig. 4 (Comparison of tensile strengths, *s/psi*, between PC extracted with different ratios)

The physical property of the PC samples tested was their tensile strength, as it is one of the most important properties of polymers that manufacturers look for. From the PC extracted, a thin, transparent PC film from each type of sample obtained using various solvent ratios (Extraction using DCM: ACE in 20:80, 30:70 and 40:60 ratios), were used to test and compare their tensile strengths. To find the breaking force of the PC samples, a Kelvin Material Tester (Fig. 3) was used. The machine pulled the 2 ends of the PC film apart until the film tore and snapped, and the breaking force, was recorded and used for further calculation of their individual tensile strengths.

The calculations performed to evaluate the tensile strengths of the types of PC are shown above (Fig. 4). To calculate the tensile strength values of the films, the breaking force was first recorded by the machine in pounds (*P/lb*). Next, the cross-sectional area was calculated by measuring the thickness (*T/mm*) and breadth (*B/cm*) of the samples and converting them to square inches. The cross-sectional area is found by multiplying the thickness and breadth. Lastly, the equation *s=P/a* was applied (*s/psi* = tensile strength, *P/lbs* = breaking force, *a/sq inches* = cross-sectional area), finding the tensile strength values for each sample.

Based on the above data, it was found that the average tensile strength value of the obtained PC films across different solvent extraction ratios was approximately 1893 psi, with 30:70 having the highest value of 1969 psi. On the other hand, commercially-manufactured PC, in comparison, has an average tensile strength of 9000 psi. The recorded tensile strengths may be inaccurate due to the extremely thin thickness of our samples. Thus, the PC extracted has lower tensile strength than commercial PC, another possible factor responsible for the weakened or degraded PC samples could be the use of solvents to recycle the PC, which may reduce the chain length, and in turn, the tensile strength. The data consisting of the value of tensile strength for PC reinforced with $BaSO_4$ nanoparticles will be further discussed below.

4.3 SEM images of $BaSO_4$ Nanoparticles

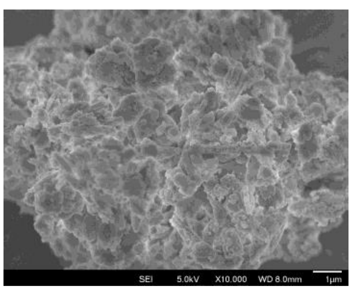

Fig. 5 (Orange extracts + $BaSO_4$)

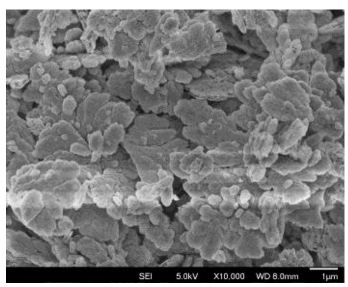

Fig. 6 (Lemon extracts + $BaSO_4$)

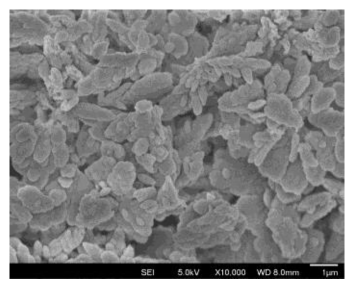

Fig. 7 (Carrot extracts + $BaSO_4$)

The $BaSO_4$ nanoparticles synthesised using fruit extracts were observed using Scanning Electron Microscopy (SEM). Fig. 5 shows the SEM images of $BaSO_4$ nanoparticles synthesised using orange extracts, likewise Fig. 6 in the presence of lemon extracts, and Fig. 7 in the presence of carrot extracts.

As seen from the images, all the particles formed clusters of size >1 micron, but the individual particles are mostly a few hundred nanometers across. The smaller size is due to biomolecules in the fruit extracts prevent the nanoparticles from coagulating. However, there is no unique shape or size of the particles, so the particles may not have been synthesised properly. Upon reflecting on past procedures, it was deduced that a possible explanation for the lack of distinct shapes and sizes of the $BaSO_4$ nanoparticles was that some of the nanoparticles had been washed out during experimental processes, when the supernatant of the centrifuged fruit extracts mixed with $BaSO_4$ nanoparticles was decanted off, thus affecting the presence and morphologies of $BaSO_4$ nanoparticles present in the samples.

4.4 Tensile strength of PC reinforced with $BaSO_4$ nanoparticles

Types of PC films (Plant extract used to synthesise $BaSO_4$ nanoparticles)	30:70, reinforced with $BaSO_4$ from carrot extract	30:70, reinforced with $BaSO_4$ from orange extract	30:70, reinforced with $BaSO_4$ from lemon extract
P/lbs	3.2	2.6	5.3
a/sq inches	0.00152	0.0012	0.00235
s/psi	2105	2167	2255

Fig. 8 (Comparison of tensile strengths, *s/psi*, between PC reinforced with $BaSO_4$ synthesised with different fruit extracts)

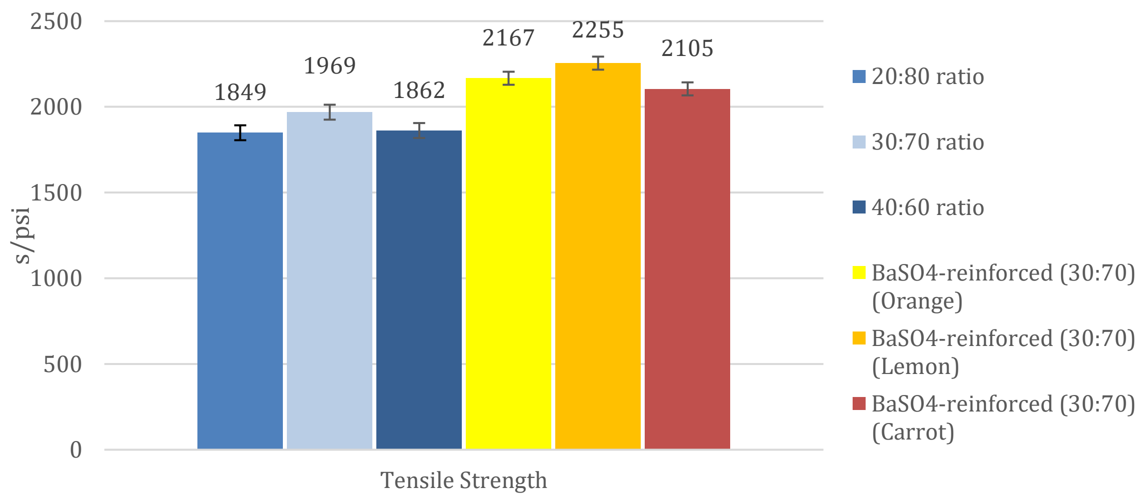

Fig. 9 (Compiled graphical comparison of tensile strengths across different types of PC)

After the PC was reinforced with $BaSO_4$ nanoparticles, the value of its tensile strength, was calculated, tabulated (Fig. 8), and represented in a graph (Fig. 9). From the graph, we can see that $BaSO_4$-reinforced PC indeed has a higher tensile strength than regular PC, and hence allows for the deduction that $BaSO_4$ nanoparticles does have a positive impact on the tensile strength of the PC, showing that PC synthesised together with $BaSO_4$ nanoparticles are able to possess enhanced properties. However, it may have an impact on transparency. Since the plastic cannot form a transparent sheet consistently, it is difficult to observe the effects on transparency.

Comparing the $BaSO_4$ nanoparticles synthesised using different fruit extracts (carrot, lemon, orange), it is evident that lemon extracts are most effective in synthesising $BaSO_4$ nanoparticles and is most useful in enhancement of the PC's properties, as the PC reinforced with $BaSO_4$ nanoparticles that were synthesised using lemon extracts produced the highest tensile strength value of 2255 psi, and is most useful in enhancement of the PC's properties.

5. Conclusion

It is possible for PCs to be extracted using solvents, which is a more economical and environmentally-friendly method to recycle plastics and reduce the amount of disposed plastic waste. Furthermore, the solvents from the extraction can be recycled for future use. However, this eco-friendly method of using solvents as a PC extraction process may not be feasible in the quality in terms of properties, as its tensile strength, compared to manufactured PC, is still lower.

For synthesising $BaSO_4$ nanoparticles, we have synthesised particles that are smaller in size than $BaSO_4$ synthesised without fruit extracts. Different fruit extracts apart from just carrot, orange and lemon may be used, and could have had a different impact on the shape and size of $BaSO_4$ nanocrystals, which in turn may affect its ability to enhance the properties of PC as an effective and suitable additive.

$BaSO_4$-enhanced PC also has improved properties as compared to PC without $BaSO_4$ although some qualities such as transparency may be compromised. However, PC reinforced with $BaSO_4$ may be preferred in other industries such as toys and plastic products due to its improved strength.

6. Future work

To improve the PC quality, more ways to shape the PC into desired sizes and shapes can be investigated, by using methods such as injection moulding, and there can also be further experimentation done to make the PC transparent. We can also investigate ways of recycling solvents as well as other polymers to make the process as cost effective as possible. Other Waste Electrical and Electronic Equipment (WEEE) such as computer circuit boards can also be recycled. Other useful physical properties of PCs such as UV stability and thermal conductivity can be tested using larger quantities of PC.

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