Bioplasticiser and Palm Oil

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INTRODUCTION

A plasticiser is a substance (typically a solvent) added to a synthetic resin to produce or promote plasticity and flexibility, and to reduce brittleness. Thus, a plasticiser is chemically defined as a substance or material incorporated into another material (usually plastic or elastomer) to increase its flexibility and workability (Krauskopf, 2009). Plasticisers have been unknowingly used in everyday life for decades. Water, for example, is a form of a plasticiser that is used by potters for moulding clay, by painters for calcimine, and by boat builders and carpenters for bending wood (Deanin, 1986). In addition, vegetable oils are used to reduce the brittleness of resins in paint, foot oil as a permanent softener for leather, and lactates in casein paint. In the 1840s, scientists discovered cellulose nitrate which is the first polymer that has been widely used in industry. Shortly after this development, camphor, a type of white and waxy solid chemical, became the plasticiser of choice for cellulose nitrate (Graham, 1973). This was due to the intractable properties of cellulose nitrate which limited its application. Camphor remained the major application for cellulose nitrate in the 19th century. However, due to the undesirable odour, flammability and excessive volatility of camphor, scientists looked for an alternative. This was how phthalate, a white solid compound, was introduced. (Phthalate is pronounced 'tha-late'.) The development of phthalates was in parallel with the commercialisation of polyvinyl chloride (PVC), and caused rapid growth in the industry. Applications of phthalates continued until the 20th century. Different types of phthalates were developed over time, differing in weight and performance.

Recently, researchers discovered that phthalates can cause disruption in the human hormone system. Thus, phthalates have been banned from certain applications such as for medical, toy and food uses (Samarth and Mahanwar, 2015). This led scientists to look for alternative additives that are safe to humans, which include non-phthalate compounds from renewable resources and processes. Well-known non-phthalate compounds are diesters and phosphates. However, these plasticisers may lead to adverse health effects because they are not chemically bound to the polymer and thus can leach out of the products (Massachusetts Lowel, 2011). Some researchers suggested the use of petroleum-based plastic to substitute PVC, but petroleum-based plastic needs additional additives for many applications. In contrast, plasticisers from renewable resources are made by the modification of natural oils and fatty acids (which occur in nature). These renewable resource plasticisers are also known as bioplasticisers. Bioplasticisers require modification because most unmodified oils or fatty acids are not compatible with polar polymers. These modifications include epoxidation and esterification processes, to form epoxidised vegetable oils, epoxidised fatty acids and fatty esters, accordingly. Epoxidation is a process of adding oxygen (O^{2-}) to the double-bond carbon (C=C) and forming a triangular structure. Meanwhile, esterification is a formation of ester from alcohol and acid. Both are shown in *Figure 1*. There are many arguments for petroleum-based plastic and plasticisers from renewable resources; however, only plasticisers from renewable resources will be the focus of this article.

GENERAL OVERVIEW OF PALM OIL

The oil palm produces two types of oil, palm oil and palm kernel oil, that have melting points between 33°C and 39°C. Palm oil is semi-solid at room temperature and is reddish-orange in colour. The very deep colour is due to the high beta-carotene content in the oil. Palm oil is composed of about 50% unsaturated fat and 50% saturated fat. Therefore, it can be claimed that palm oil has a balanced ratio of unsaturated and saturated fats, and it is primarily used in food products. In contrast, palm kernel oil has

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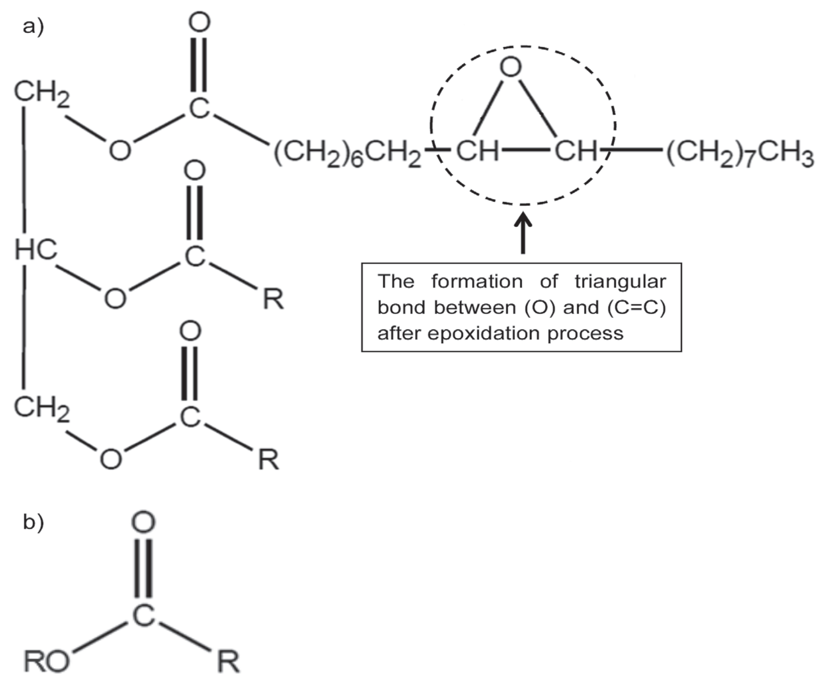

Figure 1. (a) Triangular bond formation from epoxidation process on palm oil; and (b) Esters produced from esterification process. R represents the side chains.

20% unsaturated fat and 80% saturated fat. Thus, it is mainly used in non-food applications such as in the manufacture of soaps, detergents, candles and cosmetics. Of these two types of oils, palm oil has a unique chemical composition and offers greater advantages compared with other vegetable oils. Palm oil has good resistance to heat, and thus far only 20% of its total applications is in the non-food industries. Even though the percentage is low, the added values of the products are significant for non-food applications. According to current trends, industries are starting to look towards green chemistry because of growing environmental awareness and the demand for sustainability practices among consumers, thus further bolstering the prospects for increased usage of non-petroleum oils and fats in industrial applications.

Malaysia is the second largest exporter of palm oil in the world, after Indonesia. The major consumers of palm oil are India, Indonesia, European countries and China. One of the major non-food applications of palm oil is as biofuel, an alternative fuel that is attractively safer for the environment and follows the international guidelines (Ghazali *et al.*, 2003). Heavy industries form a second important sector in palm-based applications, covering the metal processing, textile processing, degreasers and plastics industries. In the plastic industry, palm oil is incorporated into plastic additives, precursors and bioplasticisers. There may not be direct application of palm oil in these products because several processes are needed prior being applied, including epoxidation, esterification or hydrolysis.

THE RELATIONSHIP BETWEEN BIOPLASTICISER AND PALM OIL

Due to new laws and legislation, industries are now looking for alternative plastics and additives. Additional factors for the shifting of choices are stringent government regulations and health concerns from the consumers. In other words, end users are looking for safe and biodegradable substitutes. The increasing growth of the bioplasticiser industry is driven by the tight supply of harmful phthalates in developing countries. The main challenge faced by the bioplasticiser market is that bioplasticisers incur a higher cost compared with phthalate-based plasticisers. The search for sources of materials for bioplasticisers and the diversification of palm oil applications are in tandem, thus, leading to the introduction of renewable bioplasticisers from palm oil. This provides potential opportunities for the palm oil industry to widen the applications of palm oil.

Compatibility between polymers and bioplasticisers depends highly on the unsaturation level of the bioplasticisers as highly unsaturated bioplasticisers are only compatible with unsaturated polymers. Therefore, choosing the right bioplasticiser is important in order to ensure reconcilability. Unsaturation level of palm oil is determined by its fatty acid distribution. As stated earlier, palm oil has 50% unsaturated fat (fatty acids), thus the unsaturation level of palm oil is high.

A bioplasticiser is an additive that is added to a material to promote elasticity and flexibility. It is used to improve the properties and processing characteristics of polymers. A small amount of bioplasticiser can make a big impact on the polymer; thus, the polymer only needs approximately 5% of bioplasticiser in its final concentration. Generally, commercial polymers consist of different types of additives, including bioplasticiser. In order to determine the required amount of bioplasticiser, numerous studies have been done. One of the earliest studies on the use of palm oil as a bioplasticiser was by Ahmad *et al.*, in 1988.

STUDIES ON PALM OIL AS A BIOPLASTICISER

Attention to renewable resources is increasing in both industry and academic settings, in relation to the environmental aspects. Vegetable oils as one of the renewable resources which are preferred as alternatives by industry because of the relative ease of chemical transformation and universal availability. Triglycerides which are present in vegetable oils have certain reactive positions that are useful for synthetic transformation such as by epoxidation, condensation and alcoholysis. Various studies are being conducted on palm oil as bioplasticisers and their characterisation. Most of the research look into common plastics such as PVC, polyethylene (PE) and poly lactic acid (PLA) (Krauskopf, 2009).

PVC has been known for decades and has broad applications in the polymer industry. This well-known polymer is non-biodegradable and has been used since the 1930s. Like other polymers, PVC also features different characteristics with the addition of plasticisers. Earlier on in its commercialisation, PVC performed really well with phthalates. With the passing of time, the customer has started to look for eco-friendly products, and this has triggered the industry to find alternatives to phthalates. As a result, numerous studies seeking alternative polymers to PVC as well as bioplasticisers have been carried out. In 2008, a company in China patented the plasticisation of epoxidised palm oil (EPO) in PVC (CN101255143 A). EPO is the final product that has undergone the epoxidation process. The company claimed that its EPO had been successfully plasticised with improved characteristics. Nevertheless, the patented research did not stop other scientists from further exploration into this field of plasticisation. Wang *et al.* (2016) showed that the performance of palm oil plasticiser is comparable to that of a petroleum-based plasticiser, and, therefore, the use of palm oil is highly recommended as it is renewable and available at a lower cost. Also, Lim *et al.* (2015) mentioned that the palm oil works excellently as a co-plasticiser (second major plasticiser) for PVC as it changes the PVC's strength and thermal stability.

Unlike non-biodegradable PVC, polyethylene (PE) also plays a major role in the polymer industry, especially in Malaysia. According to Ratnam *et al.* (2006), the density of the polymer has been shown to gradually decline with an increase of palm oil content. Such a decline in density improves the PE toughness. Two years later, Min Min *et al.* (2008) extended their study and found that the addition of palm oil in PE produced a lubricating effect and increased its softness. Jusoh *et al.* (2013) found that palm oil is very stable in plastic products as it blended uniformly and homogenously when cooled to room temperature. Therefore, it provides a good fit for the packaging sector as an eco-friendly application. Compared with the previously described polymer, PE mixes more evenly with palm oil and does not need to undergo the epoxidation process.

Besides PE, PLA is also a biodegradable polymer that is mainly used in the biomedical field as a temporary support. PLA applications also range from the manufacture of plastic cups and plates to mulch film. Currently, PLA is widely used as a feedstock material for 3D printing. Even though PLA is a biodegradable polymer, the addition of non-biodegradable plasticisers will affect its biodegradability. The characteristics of polymer blends (PLA and EPO) have changed with the addition of the bioplasticiser EPO (Silverajah *et al.*, 2012; Chieng *et al.*, 2014; Yee *et al.*, 2014; Chieng *et al.*, 2016). Even though these scientists focused on the same polymer, PLA, their research areas were different. Nevertheless, the studies on PLA are not comprehensive enough. For now, the addition of EPO in the polymer PLA has increased in food packaging, and it has been estimated that this PLA application will be dominant by 2020. Food packaging includes the short shelf-life milk bottles, water bottles, yoghurt caps, films and trays for biscuits, fruits and vegetables, envelopes with transparent windows for bread, and also for trays and bowls for fastfood restaurants such as McDonalds (Kawashima *et al.*, 2002; Vinks *et al.*, 2004). Besides its use in food packaging, PLA has also been used for houseware and electric appliances and electronics. These include apparel, blankets, wipes, diapers, shoe-liners, furniture fabrics, compact discs (CD), computer keys, and small laptop components (Vinks *et al.*, 2004; Wolf, 2005; Platt 2006). Meanwhile, for better management of agricultural waste, PLA has been used as mulching films. As PLA is a biodegradable polymer, it has an important role in the biomedical field, especially in drug delivery systems and orthopaedic devices. PLA gets a lot of attention in the biomedical field because patients do not need to undergo a second surgical procedure to remove the devices. Thus, PLA has high potential for applications in both food packaging and the biomedical field due to its biodegradable properties.

CONCLUSION

The application of palm oil as bioplasticisers is well-known, and has been adopted in polymers since years back. Therefore, the potential of palm oil-based products as green plasticisers is undoubtedly high. Directly, it gives a neutral impact on the environment as well as a positive perspective to the palm oil industry and the economy of Malaysia. Also, it is one of the many ways to support Malaysian brands.

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