

Research Article

An Environmentally Friendly Process for the Preparation of UHMWPE As-Spun Fibres

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The extrusion of ultra high molecular weight polyethylene (UHMWPE) fibres cannot be achieved by conventional extrusion processes due to its very high melt viscosity. To overcome this limitation, UHMWPE is first dissolved in a petrochemical to form a gel before extrusion. The petrochemicals used to dissolve the polymer then need to be removed using other chemicals making the process unfriendly to the environment. This article is focused on finding an environmentally friendly, natural solution to replace these chemicals and altering the process to potentially reduce the process cost.

1. Introduction

UHMWPE is one of the strongest fibres currently available and is rapidly gaining acceptance in a variety of applications [1]. The strength of UHMWPE is 35% more than the aramid fibres on a weight to weight basis. It has the lowest density amongst the high strength fibres [2]. UHMWPE has better abrasion resistance than aramids and carbon fibres. The resistance of UHMWPE to UV radiation and highly alkaline and acidic chemicals is better than aramids, PBO (polyphenylene benzobisoxazole) and LCP (liquid crystal polymer) [3]. Owing to these physical and chemical properties, UHMWPE is widely used in applications such as bullet proof vests, load carrying ropes, cut resistant apparels, fishing lines, fishing nets, and medical inserts.

Since UHMWPE has very high melt viscosity, conventional methods of extrusion cannot be applied for the production of fibres. Therefore different methods were developed that include solid state polymerization of monomeric single crystals, simultaneous crystallization, and polymerization of monomers [4], by zone annealing, oriented crystallization of entanglement networks [5, 6], and hot drawing of gels [7–9]. A recent development is the production of UHMWPE tapes by solvent-free route [10, 11]. However the gel spinning

remains the only commercially available method of producing UHMWPE fibres. In gel spinning UHMWPE is dissolved in petrochemical solvent to form a solution, which is then extruded to form fibres. The fibres at this stage are in the form of gel fibres containing both polymer and significant amount of petrochemical solvent. In the second stage of the process the solvent is removed by utilizing a second solvent referred to as extraction solvent. Generally, paraffin, decalin, dodecane, *p*-xylene, 1,2,4-trichlorobenzene, and kerosene are used to dissolve UHMWPE [12–17]. The second stage of the solvent extraction involves solvents such as diethyl ether, *n*-pentane, methylene chloride, trichlorotrifluoroethane (TCTFE), *n*-hexane, dioxane, and toluene [13]. It is evident from the above discussion that the production of UHMWPE fibres involves significant quantities of petrochemicals. Since petroleum is a finite source, this process is not sustainable.

Paraffin was used extensively by a number of researchers [8, 9, 18–21]. It has very low volatility, but one of its components, that is, *n*-hexane, is very volatile and hazardous to human. It may cause nausea, irregular heartbeat, headache, lung congestion, nerve and brain damage, blurred vision, and impotence [22]. The second most widely reported solvent was decalin [14, 17, 23–25]. The volatile nature of decalin makes it an occupational hazard and it is a known respiratory irritant.

Decalin has been shown as carcinogen by studies conducted on rats [26]. The other chemicals used as solvent include dodecane, kerosene, and *p*-xylene. The health hazards to humans posed by these chemicals include cancer and damage to lungs and central nervous system [27–29].

The chemicals used in the second stage of solution extractions, that is, hexane, trichlorotrifluoroethane (TCTFE), and xylene, possess the risk of cancer, nephropathy, and damage to lung, central nervous system, kidney, and liver. Besides humans, these petrochemicals are also toxic to aquatic life. These chemicals are not biodegradable and have a high mobility in soil, thus contaminating ground water [28–36].

This paper reports the preliminary research carried out to find an environmentally friendly solvent for the preparation of UHMWPE fibres, which is sustainable and reduces health risks.

A wide variety of hydrocarbon solvents such as paraffin, kerosene, dodecane, and decalin have been successfully used to produce UHMWPE, the most appropriate environmentally friendly solvent to replace these petroleum solvent are natural hydrocarbon solvents such as natural oils. Given that the UHMWPE polymer dissolves at 130°C, the oils should be stable at temperatures above 130°C.

Sunflower oil, palm oil, and orange oil (terpene) were chosen for the experimental work. Sunflower oil is a natural oil with a flash point of 316°C, smoke point of 209°C, and fire point of 341°C; thus, it is very stable at temperatures around 130°C. It contains 98–99% triacylglycerols and a very small fraction of phospholipids, tocopherols, sterols, and waxes [37]. The presence of very long chains of hydrocarbons in triacylglycerols (Figure 1) makes it highly nonpolar and thus a potential candidate to be used as solvent for UHMWPE [38]. The presence of tocopherols, which are natural antioxidant, may be useful to inhibit the degradation of polymer by preventing oxidation during dissolution. Palm oil is cheaper than sunflower oil. It also contains 95% triacylglycerols with traces of other constituents such as phosphatides, sterols, tocopherols, and tocotrienols. Similar to sunflower oil it is very stable at temperatures exceeding 130°C. Orange terpene is a biodegradable natural hydrocarbon extracted from orange peel. It has been used in diverse chemical applications due to its positive environmental profile and pleasant orange aroma. The orange terpene is widely used as a cleaning solvent in place of hazardous petrochemicals. It has the status of GRAS (generally recognised as safe) by FDA (Food and Drug Administration of United States). It is not considered a carcinogen, a developmental toxicant, or mutagenic [39]. Terpene is natural hydrocarbon with carbon skeleton composed of isoprene unit ($\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$). The nontoxic and biodegradable nature combined with the presence of hydrocarbon makes it a potential alternative to petroleum hydrocarbons for the production of UHMWPE fibres.

2. Experimental

2.1. Materials. Ultra high molecular weight polyethylene Gur 4120 with average molecular weight of 5.0×10^6 supplied by the Ticona UK Ltd was used in this work. The polymer density

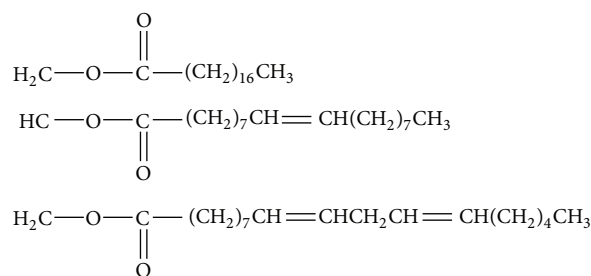


FIGURE 1: Structure of typical triacylglycerols [38].

was 0.93 g cm^{-3} , with melting point in the range of 130°C–135°C. The solvents used were sunflower oil, palm oil, and orange oil (terpene). Sunflower oil and palm oil were acquired from the local grocery store, while the orange oil (terpene) was sourced from Sigma-Aldrich. The boiling point of orange oil was 176°C. 2,6-Di-*tert*-butyl-4-methylphenol antioxidant was also supplied by Sigma-Aldrich.

2.2. Ram Extruder. ESL ram extruder capable of applying a pressure of 700 psi was used to extrude the fibres. The temperature was set at 150°C and a monofilament die was installed on the ram extruder. A water bath was placed to cool the extrudate. Water was kept at ambient temperature. The extrudate was passed through the water on emerging from the die. A winder was installed at the end of the water bath to wind the fibre on bobbin. Winder was operated at the speed of 5 m min^{-1} .

2.3. Differential Scanning Calorimetry: DSC. METTLER-TA instrument and METTLER-TOLEDO-TA89E system software were used to determine the melting point of the UHMWPE samples in powder, gel, and fibre forms. The start temperature was 20°C and the end temperature was 300°C for the scanning of all the samples. The heating rate was $10^\circ\text{C min}^{-1}$. The weight of the specimen was 5 mg in an aluminium pan.

2.4. Method. Three natural oils, sunflower oil, palm oil, and orange oil (terpene), were used to form the gel. In the experiment, first a 5% solution of oil was prepared. 1% 2,3-di-*tert*-butyl-4-methylphenol (ionol) was added to avoid oxidation. The solution was heated to 130°C with constant stirring. All the oils used in the experiments failed to produce a solution of UHMWPE; rather, they produced a clot except terpene. Thus, terpene was selected to carry out further experiments. 5% solution of UHMWPE with 1% ionol was heated to 130°C with constant stirring. On the emergence of Weissenberg effect, the gel was stirred manually for one and a half hours. The gel was then left overnight to become stable at room temperature. It was then cut in small pieces (approximately 5 mm^3) and fed into the barrel of ram extruder. The barrel was heated to 150°C. The gel was left for 10 min in preheated barrel to melt the gel evenly before extruding. The extrudate was quenched by passing it through a 10 cm air gap. The extrudate was then passed through a

water bath at ambient temperature at a speed of 2 m min^{-1} . After quenching, the filaments were wound onto the bobbin. The traces of the terpene were removed by leaving fibres for 48 hr under ambient conditions.

3. Results and Discussion

UHMWPE as-spun fibres were produced by utilizing terpene as an alternative to petrochemicals. The use of terpene oil as an alternative to petrochemicals provides an environmentally friendly process. Since it is from a renewable source (i.e., orange peel), it is sustainable. It is by-product of the orange juice industry and thus does not strain the natural resources and does not put any pressure on food supply. In the conventional gel spinning process, removal of spinning solvent is carried out by utilizing a secondary solvent, while in the present work the solvent was removed by passing the fibres through the water bath. Due to the lower temperature of water bath the temperature of the fibres dropped which caused phase separation. The phase separation is a common characteristic of the gel. For a polymer to dissolve into a solvent or remain as a homogeneous solution, it must satisfy the following equation [12]:

$$\Delta F_m = \Delta H_m - T\Delta S_m, \quad (1)$$

where

ΔF_m = Free energy of dissolution,

T = Absolute temperature,

ΔH_m = Heat of dissolution,

ΔS_m = Entropy of dissolution.

For a nonpolar polymer dissolving into a nonpolar solvent, the situation where $\Delta H_m \geq 0$ and $\Delta S_m > 0$ can only occur when T is high enough to facilitate $\Delta H_m < T\Delta S_m$. A homogenous solution of a nonpolar polymer into a nonpolar solvent prepared at a high temperature gets unstable when the temperature decreases. The balance of the system is disturbed resulting in the coagulation of polymer from solution.

UHMWPE is a nonpolar polymer with high molecular weight. It dissolves at above 130°C . As discussed previously, the process of dissolution meets $\Delta H_m < T\Delta S_m$ during the spinning process, when the extrudate entered the water bath at ambient temperature, which was much lower than the temperature of phase separation. The phase separation occurred and solvent left the solidified fibres to enter the water. The phase separation continued when the filaments were kept at room temperature. It was found that the solvent could be removed from the filaments by passing through the water and leaving at room temperature. To investigate whether the solvent is completely removed from the fibres, DSC thermographs of the polymer powder, gel, and dried fibres were taken which are shown in Figures 2, 3, and 4, respectively.

In the DSC thermograph of the UHMWPE powder in Figure 2, the peak at 137°C corresponds to melting of the polymer. Figure 3 shows the DSC thermograph of gel prepared with terpene. The first peak at 110°C indicates the melting

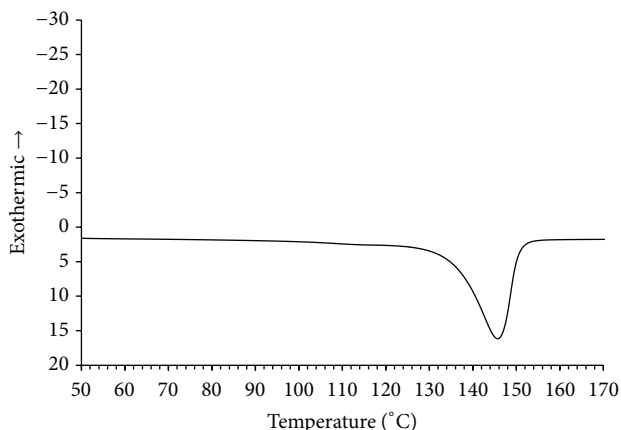


FIGURE 2: DSC thermograph of UHMWPE powder.

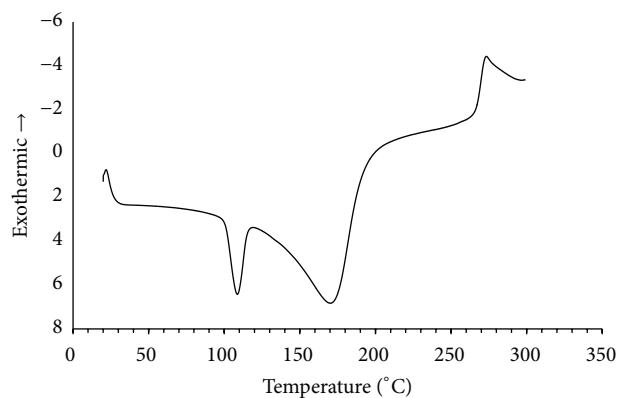


FIGURE 3: DSC thermograph of gel.

point of the polymer which is lower than that indicated in Figure 2 due to the imperfection in the crystal of polymers caused by the gel formation and the presence of terpene [14]. The second peak at 170°C indicates the boiling point of the terpene. The two different peaks in Figure 3 indicate the presence of polymer and solvent. The DSC thermograph of UHMWPE fibre shown in Figure 4 shows one peak at 138°C indicating the melting point of the UHMWPE, which increased from 110°C in the gel form to 138°C in the fibre form; the absence of second peak in the fibre shows the complete removal of the terpene from the fibres.

A comparison between conventional gel spinning process and terpene based modified gel spinning process is shown in Figure 5. Both processes involve the preparation of solution. In the second stage of both processes, the solution is heated to dissolve the polymer. Polymer solution is then extruded and quenched to form gel-like fibres. The modified process deviates from the standard one at this stage. In the case of conventional gel spinning process a separate solvent extraction process is performed by using evaporative solvents such as n-hexane, hexane, cyclohexanone, xylene, gasoline, and toluene, which adds to the cost of the process. Hence, the elimination of the solvent extraction process not only

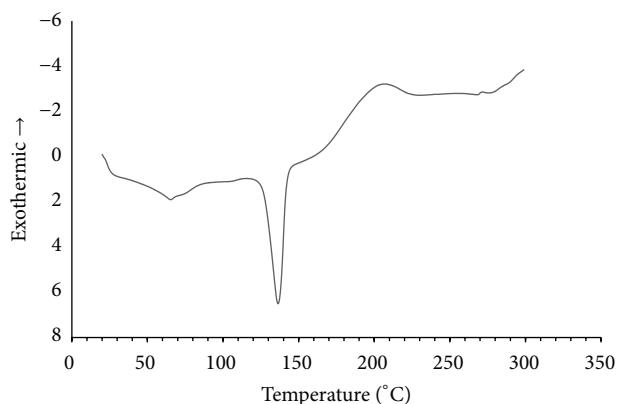


FIGURE 4: DSC thermograph of UHMWPE fibre.

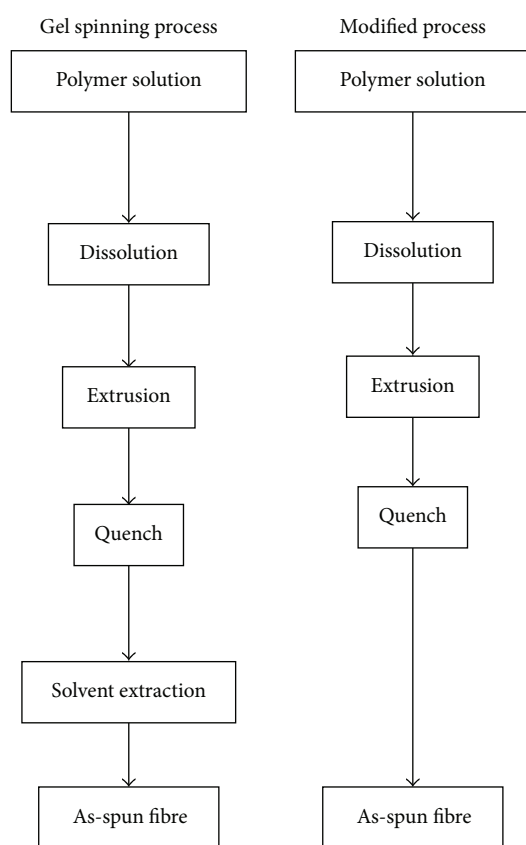


FIGURE 5: Comparison between conventional gel spinning process and modified gel spinning process.

eliminates the use of hazardous chemicals, but also reduces the cost of the process.

4. Conclusions

Terpene was successfully used in place of petrochemicals to produce UHMWPE as-spun fibres. Terpene, which is a natural oil extracted from orange peel, can replace the petrochemicals previously used in the processing of UHMWPE. As a natural oil, it is obtained from renewable resources.

Unlike other sustainable alternatives to petrochemical, such as biodiesel, which are extracted from edible products, it is extracted from the orange peel; hence, it not only is sustainable, but also does not put pressure on the human food supply. Since terpene is biodegradable, the disposal of terpene does not require special treatments, hence reducing the cost involved to dispose it.

The terpene-based process is more user friendly than the previously reported process due to utilisation of the terpene as solvent instead of petrochemicals. FDA has given terpene the GRAS status. Terpene is not considered a carcinogen, a developmental toxicant, or mutagenic. The safer nature of the terpene makes the process less hazardous to the people working in the production of the fibres, hence making the process safer than the previous processes.

The petrochemical solvents used in traditional gel spinning of UHMWPE work only as a medium to assist in the spinning of the fibres from polymer powder. After fibres have been extruded, the solvents need to be removed which involves the use of a secondary petrochemical solvent. In terpene based gel spinning process, the extraction of solvent takes place during the water quenching of the fibre and does not therefore require a separate removal process. This eliminates the need for an extraction stage employing additional solvents. The elimination of the secondary solvent not only reduces the cost associated with it, but also eliminates the other three major concerns regarding sustainability and environmental and health hazards. The complete elimination of the extraction stage can also result in the reduction of labour and energy costs associated with this stage. The process is simple and uses standard extrusion equipment in contrast to the previous process, which requires special equipment [14, 40].

Conflict of Interests

The authors declare that there is no conflict of interests regarding to the publication of this paper.

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