

NOTE

A New Method for Preparation of Lightweight Ultrahigh Molecular Weight Polyethylene (UHMWPE) Foam

INTRODUCTION

Ultrahigh molecular weight polyethylene (UHMWPE) due to its solution properties upon shearing has been of extensively increasing interest. The crystallization in the shish-kebab structure possessed an ultrahigh modulus.¹⁻⁴

In general, solutions of UHMWPE, when rapidly stirred, would crystallize into a shish-kebab structure consisting of a central strand with chain-folded kebab crystals growing normal to it. This type of gelation required an elongational flow field.¹⁻⁴ To form a gel, a three-dimensional network is needed. Entanglement and interlamellar and interfibrillar links were involved in the gelation.¹⁻⁵ Foams could be obtained from the gels if the solvent was removed without elastic collapse of the swollen polymer.⁵ However, the foams were rather an irregular shape and did not appear in bulk form. In this study, UHMWPE foam with an average density of 0.11 g/cm³ was obtained by extracting the solvent xylene with alcohol.

EXPERIMENTAL

UHMWPE powder, 2.00 g (supplied from Hoechst and specifications given in Table I), 0.5 mL antioxidant solution (stock solution of mixture of Cyanox LTDP and

Table I Properties of UHMWPE Samples, from the Producer Company

Property	GUR 412	GUR 415
Density (g/cm ³)	0.94	0.93
M_w	4×10^6	6×10^6
Yield stress (MPa)	22	21
Ultimate tensile stress (MPa)	41	44
Elongation at break (%)	450	450
Melt index (MFI) 190/15 (g/10 min)	< 0.1	< 0.1

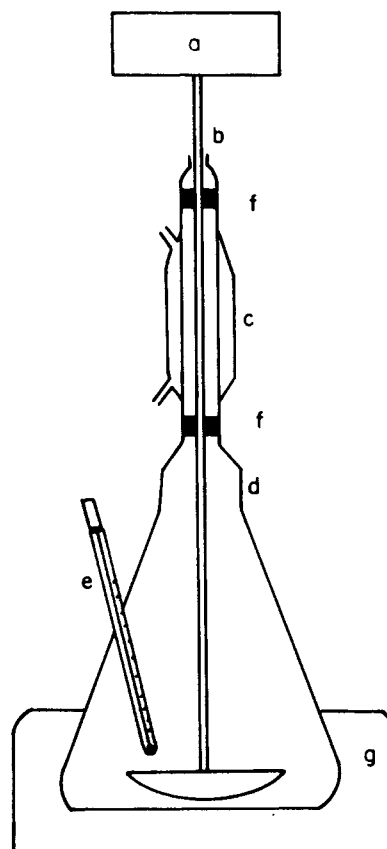


Figure 1 Experimental apparatus for preparation of UHMWPE gel: (a) motor; (b) Teflon stirrer; (c) condenser with a 55/44 quick fit; (d) 500 mL Erlenmeyer; (e) 200°C thermometer; (f) stirrer supports; (g) heating jacket.

Cyanox 1735, 0.4 g of each, in 100 mL xylene was used as an antioxidant in preparation of foams to protect UHMWPE from thermal degradation), and 100 mL xylene was placed in an Erlenmeyer as shown in Figure 1.

The mixtures were stirred at three different speeds, 400, 740, and 1130 revolution per minute (rpm), and heated continuously up to the boiling temperature of xylene (137°C) until a clear and highly viscous solution was obtained. The total time of this procedure was about 20 min.

During the preparation process of UHMWPE gel, as the temperature approached the melting point of the

Table II Amount of Solvent Absorption of Foams

	THF (Solvent)		Acetonitrile (Solvent)	
	GUR 412	GUR 415	GUR 412	GUR 415
Absorption g solvent/g foam	4.71	5.28	3.23	3.70

polymer, the solution became very viscous and ultimately gelled around the stirrer. On heating, the first sign of melting occurred at 105°C, and the sample shrank markedly. Then, it was followed by expansion, at which probably most of the PE not associated with fibers had melted. At a temperature about 105°C, the solution was not clear, but as the temperature of the solution approached the boiling point of xylene (137°C), it became clear and transparent. At 137°C, only thin strands of PE might exist. Since it is known that nascent UHMWPE crystallizes in an extended chain and can be expected to superheat, an oriented structure exists even after the melting point.

This clear solution was transferred into glass tubes of size 4 cm in diameter and 15 cm in height. Then, they were immediately placed to be quenched in an oven at 120°C for 15 min. Afterward, the temperature was reduced to 60°C and the samples were precipitated within 20 min. The excess xylene was removed by applying pressure (by putting weights of 200 g) on the gel while temperature was decreased to ambient. Absolute ethanol was added on

these gels, and they were left in absolute alcohol to remove the remaining solvent. The alcohol-xylene solution was changed every 24 h and fresh alcohol was added. This process was repeated seven times. Finally, ethanol was removed in a vacuum oven at 70°C for 36 h.

Foams were found to be highly porous and capable of absorbing amounts of liquid greater than three times of their own weights as given in Table II. Two solvents, tetrahydrofuran and acetonitrile, were used. After leaving the foams in these solvents for 24 h, the surfaces of the foams were cleaned by a tissue to remove the extra solvent and weighing followed at room temperature.

Thermal properties of foams were analyzed in a Perkin-Elmer Model 4 DSC. Scanning electron microscope (SEM) observations of the fractured surface of the foams were made at various magnifications using the JEO4 JSM.6400 SEM after protective gold coating. The samples were fractured by a hammer after cooling to the liquid nitrogen temperature (-196°C) in order not to damage surface morphology.

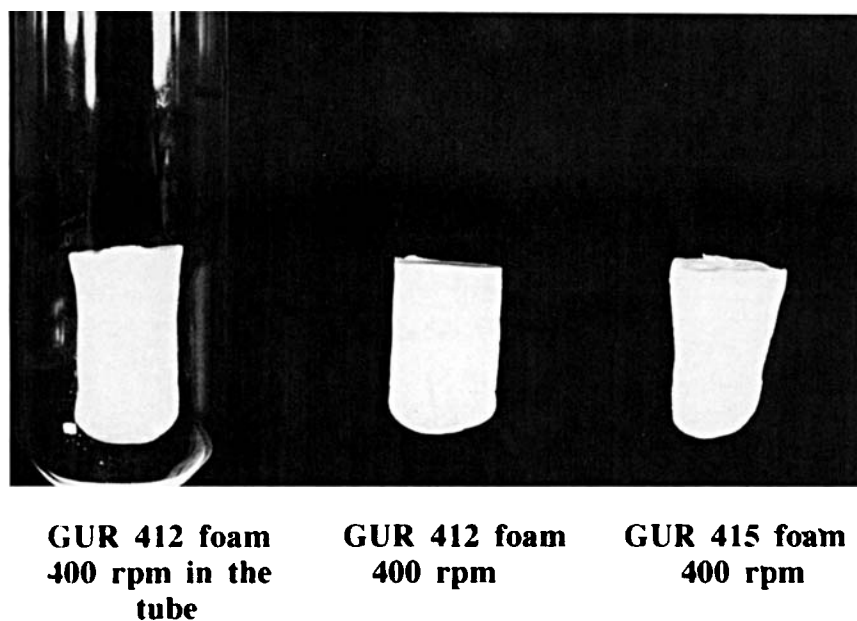


Figure 2 Shape and relative shrinkage of the foam; on the left, the foam stands inside the test tube.

Table III Melting Points and Enthalpy of Melting of Received UHMWPE Powders and Foams Prepared at Different Stirring Speeds

	GUR 412		GUR 415	
	T_{mp} (°C)	ΔH (J/g)	T_{mp} (°C)	ΔH (J/g)
Received Powder	140.0	165.9	140.8	147.8
400 rpm	136.9	188.1	138.9	186.2
740 rpm	137.4	210.4	138.1	188.2
1130 rpm	136.5	209.8	137.2	192.0

RESULTS AND DISCUSSION

Foams were characterized by density measurement and thermal and SEM analysis. Foams were obtained having an average density of 0.11 ± 0.02 g/cm³. In Figure 2, the shape and relative shrinkage of the foam are given after complete drying of the gel. When the size of the hot gel

was compared to the size of foams obtained, the shrinkage was found to be approximately 60% (by volume). This can be seen on the left side of Figure 2 where the foam stands in the glass tube. Note that the shape of the foam was retained in the form of the glass tube. The lower molecular weight UHMWPE, GUR 412, appears to be more successful in retaining the shape of the glass tube in all cases.

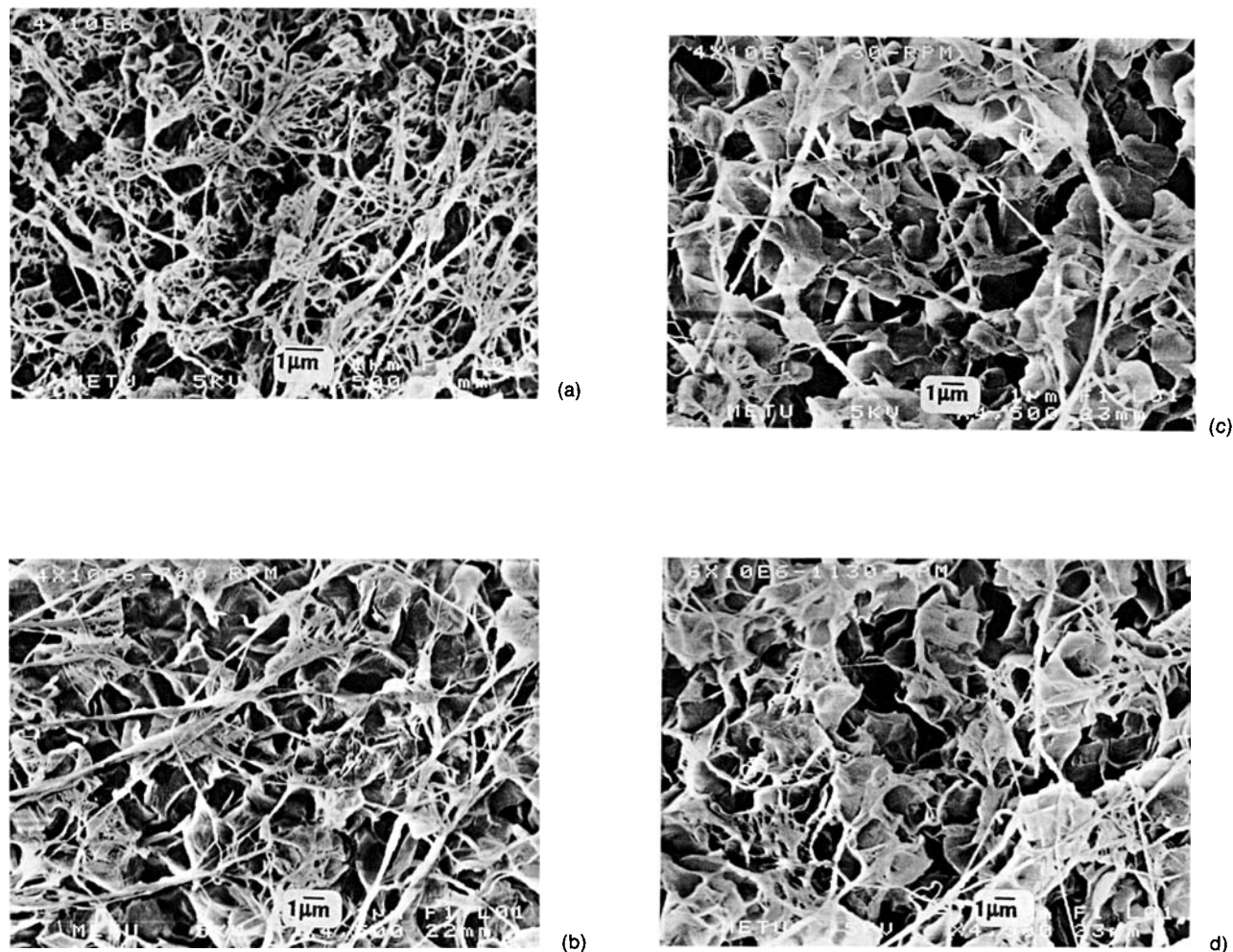


Figure 3 Morphology of fractured GUR 412 foams stirred at (a) 400, (b) 740, (c) 1130 rpm, and (d) morphology of fractured GUR 415 foam stirred at 1130 rpm.

The melting points of pure powder GUR 412 and GUR 415 were found to be about 140 and 141°C, respectively. The highest melting temperature in pure UHMWPEs could be obtained from the first scan of the received powder.⁶ The change in melting points and enthalpies of melting are given in Table III. The stirring speed did not affect the melting points of the foams but a distinguishable decrease was observed when they were compared to the virgin powders. In all cases, the melting points were found to be very sharp and did not contain any higher melting point tail. On the other hand, the stirring speed affected the enthalpies of melting and morphology of foams (see micrographs). The enthalpy change of melting was found to increase with stirring speed, indicating enhancement in crystallization. The high melting points of foams indicate the existence of a high-modulus extended fiber formation. However, it is difficult to state the presence of a shish-kebab structure, if any, in the foams due to our thermal treatment.

SEM results support the thermal analysis data. Extended fibers, although not resolved to higher magnifications due to the high power of electron impact on the rough surface of the foams, can be followed from the foam prepared at low stirring speed (400 rpm) [Fig. 3(a)] to the high speeds of 740 rpm [Fig. 3(b)] and 1130 rpm [Fig. 3(c)] for GUR 412 foams. This gradual change in structure was also observed for GUR 415 foams [Fig. 3(d)]. The existence of extended fiber and chain-folded lamellae connecting each other can be seen in these figures.

Low-density (0.11 g/cm³) UHMWPE foams, but higher in density compared to the foams of Matthews and Hoffman,⁵ which varied from 0.02 to 0.05 g/cm³, were prepared. In addition to this, the experimental procedure developed in our laboratory provides the use of simple and safe solvents; especially, it was useful during the removal of the

solvent from the foam structure. A network formation through the extended fiber was seen in the SEM microphotographs. With changing stirring speeds, the morphology was found to be affected. The foams were tough and rigid enough and highly absorbable and can be machined easily.

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