The Preparation and Characterization of Hydrophilic Macroporous Foams from Water Soluble Polymers Grafted Ultra-High Molecular Weight Polyethylene

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ABSTRACT: Macroporous foams of water soluble polymers grafted ultra-high molecular weight polyethylene (UHMWPE) were obtained by precipitation of hot xylene gel solutions in ethyl alcohol. The water soluble monomers used for grafting were acrylic acid (AA), methacrylic acid (MAA), acrylamide (AAm), N-vinylpyrrolidone (NVP), and N-N-di-methyl acrylamide (NNDAm). The morphology of the foams was investigated using the scanning electron microscope (SEM). Significant changes in the morphology and pore size were observed among the foams depending upon the type of grafting water soluble polymers. The porosity of the foams was uniform and varied from 1 to 10 μm. The percentages of the free volume and water uptake of the foams were measured. The foams obtained from grafted UHMWPE had an appreciable water uptake capacity and water could pass through them compared with the water repelling pure UHMWPE foams. The poly(NNDAm)-grafted UHMWPE yielded markedly better foams than the others. The water soluble polymer-grafted conventional polymers posses the characteristics of hybrid material where hydrophobic and mechanically strong UHMWPE make up a strong backbone and hydrophilic hydrogel affords biocompatibility. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

It is well-known that the great majority of polymers or polymer-based materials are water insoluble, and indeed they are usually required to be water resistant. However, the relatively small in number, but important class of polymers are water soluble polymers which have different features and applications. These materials are often referred to collectively as "water soluble gums" or "water soluble resins."[1] The solubility of these materials in water is an important feature in their applications in certain areas. Therefore, the combinations of the properties of the two different classes of these polymers (hydrophobic and hydrophilic) can provide many unique properties.

Ultra-high molecular weight polyethylene (UHMWPE) have various superior properties in terms of melt viscosity, impact strength, stress-cracking and abrasion resistances, and thermal stability to its low molecular weight counterparts, and like all polyethylenes, it has very good resistance to aggressive media except for strong oxidizing acids.[2,3] Over the last decades,

UHMWPE has been used in many areas ranging from artificial hip joints to pyrolysis studies.[4,5]

The two most important characteristic properties of polyethylenes are their light weight and considerably high enough mechanical strengths. These features make UHMWPE a good choice as a backbone polymer for the grafting of water soluble polymers. The conventional polymers grafted with water soluble polymer posses the characteristic combination of hydrophilicity and hydrophobicity and find many applications at least in laboratory scale as reviewed by Nasef and Hegazy such as in separation processes (dialysis, electrodialysis, ion-exchange, gas separation), energy conversion (batteries, fuel cells), solid state sensors (pH, temperature, light, humidity, chemical, and biological agents), biomedical and biological studies (glucose biosensor, controlled drug release, immobilization of enzymes, blood purification, biomaterial), environmental (removal of heavy and toxic and separation of precious metals), and miscellaneous applications (electrophoresis, catalysis, semiconductor

Table I. Grafted UHMWPE Powder Samples

UHMWPE	% Graft				
	Poly(AA)	Poly(MAA)	Poly(AAm)	Poly(NNDAAM)	Poly(NVP)
GUR 412	35.9	24.7	32.0	39.6	38.3
GUR 415	41.9	14.9	20.3	33.1	24.3

assemblies).[6–8] Among the water soluble monomers, acrylic acid (AA) is the most frequently used grafting monomers on hydrophobic polymers. The materials and membranes obtained by grafting of AA, methacrylic acid (MAA), acryl amide (AAm), N-N-di-methyl acrylamide (NNDAm), and N-vinylpyrrolidone (NVP) onto mechanically and chemically strong polymer backbones were prepared by various means. And they found many applications in medicine, various filtration processes, and some other related areas.[9–11]

The stable UHMWPE foams obtained from their hot gel xylene solutions were previously obtained by Aydinli and Tincer.[12] Furthermore, pyrrole was successfully polymerized in the interior of the UHMWPE foam by chemical means, and thus conducting polymer composite was obtained.[13] Also, the grafting of five different water soluble monomers on UHMWPE resin powder by the direct radiation method was also described by Aydinli.[14]

This study covered the preparation of foams from the resins of grafted UHMWPE by the technique described earlier.[12] But, some detailed examinations and assessment were also performed in terms of some factors such as the dimensional stability, pore size, density, hydrophilicity, free volume, and water uptake capacities of the foams to offer some practical techniques regarding the preparation of the foams.

The foams obtained from grafted UHMWPE in this study may have potential applications in aqueous mediums such as dialysis, filtration industries, and especially humans, e.g., to serve as tissue scaffolds. Also, some other possible applications may be realized due to increased dyeability and electrical conductivity when foam materials are wet.

EXPERIMENTAL

Materials
UHMWPE. UHMWPE samples were supplied by Hoechst (now Aventis) GUR 412 (M_w = 4 Million) and GUR 415 (M_w = 6 Million) in powder form and contained corrosion inhibitor and used as received. Their melting points are 141°C.

Grafted UHMWPE. The previously obtained grafted UHMWPE powder samples were used in this study, which were given in Table I where the grafting percent, grafting water soluble polymers, and backbone grafted UHMWPE were specified. These grafting ratios used in study were the highest in amount, which had been obtained in our previous study.[14]

Preparation of Foams
The foams were prepared from both virgin and grafted UHMWPE. The complete procedure of the production of the stable foams had been described previously.[12] In the previous study, briefly, the UHMWPE-xylene mixtures were simultaneously heated and stirred up to the boiling point of xylene (137°C) until clear and highly viscous solutions were obtained. After these solutions were transferred into cylindrical glass tubes of 4 cm in diameter and 15 cm in height, they were quenched in an oven at 120°C and then the temperature was reduced to 60°C. Then, the obtained gels were precipitated by adding absolute ethyl alcohol and pouring it once in every 24 h, which lasted 7 days until all the xylene was removed from the gel. Finally, ethyl alcohol was removed from the structural body of the gel by a vacuum oven, which resulted in porous UHMWPE foams. Apart from these, to control the structure, morphology, porosity, and properties of the foams obtained from the virgin GUR 412, various weight/volume percentages of the GUR 412/xylene (0.5, 1.0, 2.0, 2.5, 3.0, 4.0 w/v %) were used at three stirring speeds: 400, 740, and 1130 round per minute (rpm). Along with ethyl alcohol, the other precipitating solvents such as isopropanol, acetone, diethyl ether, n-propanol isobutanol, and n-butanol were also used separately in this study. In addition, not only the grafted UHMWPE but also the virgin UHMWPE added grafted UHMWPE powders were used to obtain better stable foams. The percent ratios of the grafted UHMWPE to the virgin UHMWPE are 100, 80, 60, 40, and 20, respectively. Generally, throughout the study, 2.5 g of the virgin and/or the grafted UHMWPE, 100 cm³ xylene, 740 rpm stirring speed, and ethyl alcohol were used for the production of the foams.

Observation of Structure and Morphology of Foams
The bulk structure and morphology of the foams were observed and examined at various magnifications in scanning electron microscope (SEM), JEOL-SEM6400 (Tokyo, Japan). The foams were fractured in liquid nitrogen and coated with protective gold preceding the observation with the SEM.

Measurements of Water Uptake, Free Volume, and Density of Foams
The water uptake and free volume measurements of the grafted UHMWPE foams were performed on the foams cut in cylindrical shapes with a thickness of 1–2 mm and these cut foams were weighed (w_1). Then, water was forced through the foams by suction for 4 h to prevent any air bubbles from trapping in the foam structure and also to allow water to reach deep pores of the foam for thorough wetting. This resulted in true measurement of the water absorption capacity of the foams. Then the foams were cleaned by a tissue paper to remove extra water and weighed again (w_2). Water uptake percentages which were calculated with the following equation and recorded as the first water uptake:

$$\% \, \text{water uptake} = \frac{w_2 - w_1}{w_2} \times 100 \qquad (1)$$

Table II. Densities (g/cm^3) of Pure GUR 412 Foam Prepared at Various Weight Percentages and Stirring Speed

% w/v of GUR 412-xylene	Stirring speed (rpm)		
	400	740	1130
1.5	0.19	0.27	0.15
2.0	0.19	0.15	0.12
2.5	0.12	0.13	0.12
3.0	0.10	0.11	0.11
4.0	0.11	0.09	0.13

After these samples were dried completely under vacuum, the samples were made to absorb water again with the same method, which is called the second water uptake of the foams.

For the free volume measurements, structurally proper and big parts of the foams as big as possible were taken and weighed (w_1). Then, these foams were immersed in an easily penetrating and volatile liquid CCl_4 which has relatively low surface tension. After a certain time, 5 to 6 min, the sample removed and the surface of the foam was dried by tissue paper in the possible shortest time and weighed immediately again. The weight was recorded as w_2. The weight difference ($w_2 - w_1$) was converted into the volume of CCl_4 using its density. The volume of CCl_4 is actually the absolute free volume of the foams. After the foams were dried under atmospheric condition, they were compressed using hot platen press, and thus uniform films were obtained. The volume of the obtained film (V film) was calculated by drawing it on a graphical paper to find the area and then multiplying the thickness of the film with its area. The sum of ($V\,CCl_4$) and (V film) is the total volume of the foams. The free volume percent of the foams was calculated using the following equation:

$$\% \quad \text{free volume} \quad = \frac{V\,CCl_4}{(V\,CCl_4 + V\,\text{film})} \times 100 \qquad (2)$$

It is very difficult to find exactly the free total volume of the foams both with the displacement of liquid and dimensional mathematical calculation; therefore, these two methods were not used in this study.

Density measurements were performed just for the foams obtained from the virgin GUR 412 by dividing their masses with their volumes, Table II.

RESULTS AND DISCUSSION

Structure and Properties of the Foams

Pure UHMWPE. The average densities of the pure GUR 412 UHMWPE foams produced at different stirring speeds and the weight percentage of the GUR 412 in the xylene were presented in Table II. For 0.5 and 1.0% solutions, stable gels could not be obtained probably due to insufficient UHMWPE amount to preserve the structure of the gel which was attained during the precipitation of the hot gel. For other cases, the densities were around 0.12 g/cm^3. But, some of the foams obtained from 1.5 and 2.0 % solutions have higher densities (around 0.20 g/cm^3). This could be due to the collapse of the swollen structure of the

gel before the xylene was removed with ethyl alcohol with subsequent drying in a vacuum oven. However, foams could not be obtained from any w/v UHMWPE/xylene solution higher than 4.0% due to the high viscosity of the gel solution and strong adherence of the gel to the wall of the glass apparatus which inhibited the laboratory scale handling of the gel solution. Possibly, foams having lesser density could have been produced despite an added higher amount of solid polymer to the xylene if the formed chain entanglements of the UHMWPE strands resembling shish-kebab structure under elongational flow field had preserved easily their three dimensional form with the removal of the xylene in ethyl alcohol.

As precipitating liquids, isopropanol, acetone, diethyl ether, n-propanol, isobutanol, and n-butanol other than ethyl alcohol were used to cause changes in the pore size and to increase the dimensional stability of the foams. All of these liquids were miscible with xylene and they were nonsolvent for PE. The more polar organic solvents are the better nonsolvents will be for PE. As water is not miscible with xylene, it cannot be used. Also, n-butanol, isobutanol, and n-propanol produced highly shrunk foams due to incomplete removal of xylene and the difficulty of their evaporation in the proceeding vacuum oven drying. Isopropanol, acetone, and diethyl ether worked well probably due to their high vapor pressure, producing foam densities of 0.12, 0.09, 0.15 g/cm^3, respectively for 2.5 % w/v UHMWPE-xylene mixtures at 400 rpm. It was observed that acetone produced lower density foam compared with the other solvents (ethyl alcohol produces 0.12 g/cm^3). It is obvious that the density of the foams decreases with increasing weight percentage of the UHMWPE.

All the SEM photographs of the fractured surfaces of the pure foams obtained from 1.5, 2.5, 4.0 % w/v solutions at 400, 740, 1130 rpm, respectively precipitated in ethyl alcohol, and the photographs of 2.5% w/v solutions at 400 rpm precipitated in isopropanol, acetone, and diethyl ether were examined to determine the effects of the UHMWPE percentages in xylene solution, stirring speed and precipitation agent on the morphology and mechanical properties of the foams. As the morphology and apparent mechanical properties of the pure foams do not change sharply with the stated variables, only the foam
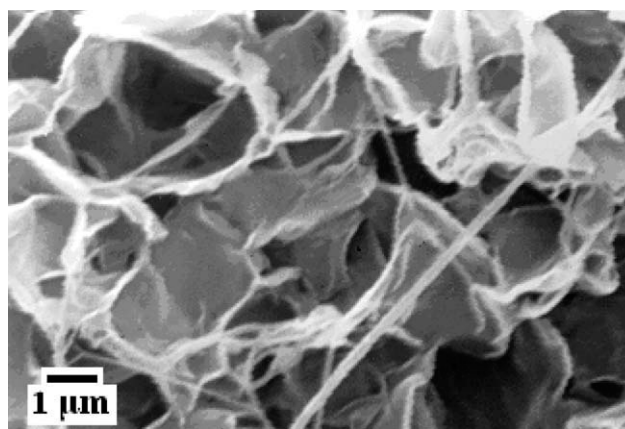
Figure 1. Morphology of fractured foam obtained from virgin GUR 412.
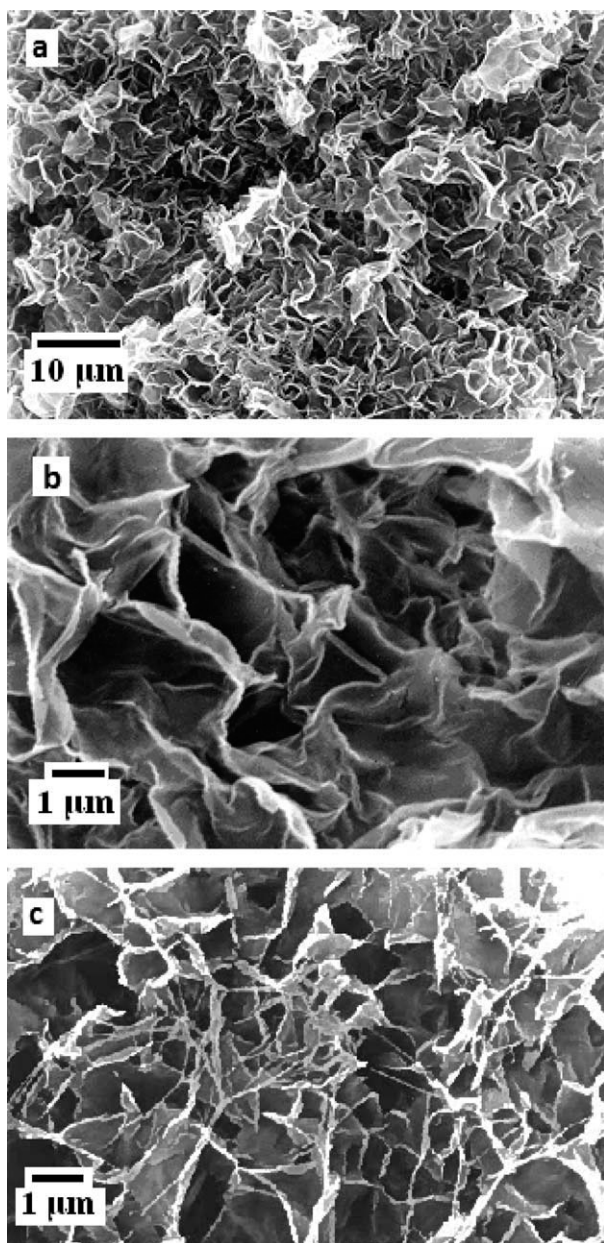
Figure 2. (a) and (b), Morphologies of fractured foam obtained from 37% poly(NNDAm)-grafted GUR 412 at two magnifications and (c) foam obtained from mixture of 60% (37% poly(NNDAm)-grafted GUR 412) and 40% (virgin GUR 412).

precipitated in ethyl alcohol obtained from 2.5 % w/v solution at 400 rpm was given in Figure 1 just to compare those pure UHMWPE foams with the grafted UHMWPE foams.

Grafted UHMWPE. The SEM photographs of the grafted UHMWPE foams were given in Figures 2–7 where Figure 2(a–c) for poly(NNDAm), Figure 3(a,b) for poly(NVP) and Figure 4(a,b) for poly(AA), and finally Figure 5(a,b) for poly(MAA)-grafted foams, respectively.

The morphology of the foams can be examined by considering the two variables; one is the percent added virgin UHMWPE

into grafted UHMWPE and the other is the change in the grafting monomer. The effect of the former on the morphology, apparent stability, and strength of the foams were very clear. For instance, in the case of the absence of the added virgin UHMWPE, it is impossible to see the fibrillar structure which results in poor apparent mechanical properties. In addition, some of the highly grafted foams can be pressed between fingers and they are easily fractured, but some other, like the poly(-NNDAm) grafted one, just deforms. However, the pore size of the foams becomes uniform due to complete flake-like morphology as seen in Figure 2(a–c). With the addition of the virgin UHMWPE, the occurrence of the fibrillar structure increases [Figure 2(c)] and the foams become as strong as the virgin UHMWPE while they still keep a significant water uptake capacity (20–30%).

The effect of the latter, the grafting monomer, is less clear concerning the morphology. Yet, poly(NVP) and especially poly(NNDAm)-grafted UHMWPE resins produced more stable foams with bigger pore size than the poly(AA), poly(MAA) and poly(AAm) grafted ones. If the chemical structures of the water soluble polymers used in this study are examined, the poly(NNDAm) and poly(NVP) cannot make hydrogen bonding and crosslinking reaction under normal conditions. Thus, they allow UHMWPE chains to behave freely as if they were alone in solution or under hot compression. In fact, the morphology of the foam obtained from the pure poly(NNDAm) (Figure 2) grafted
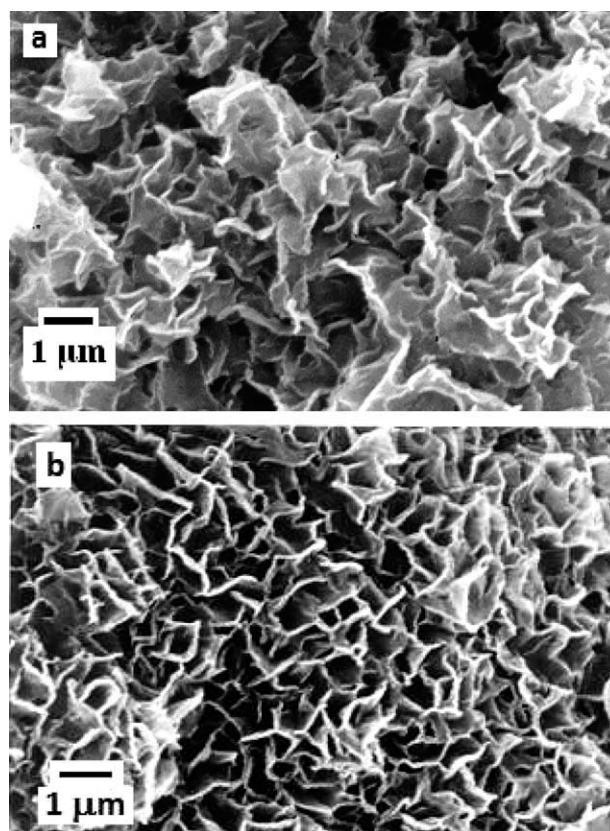
Figure 3. (a) and (b) Morphologies of fractured foam obtained from 38.3% poly(NVP)-grafted GUR 412 and 415, respectively.
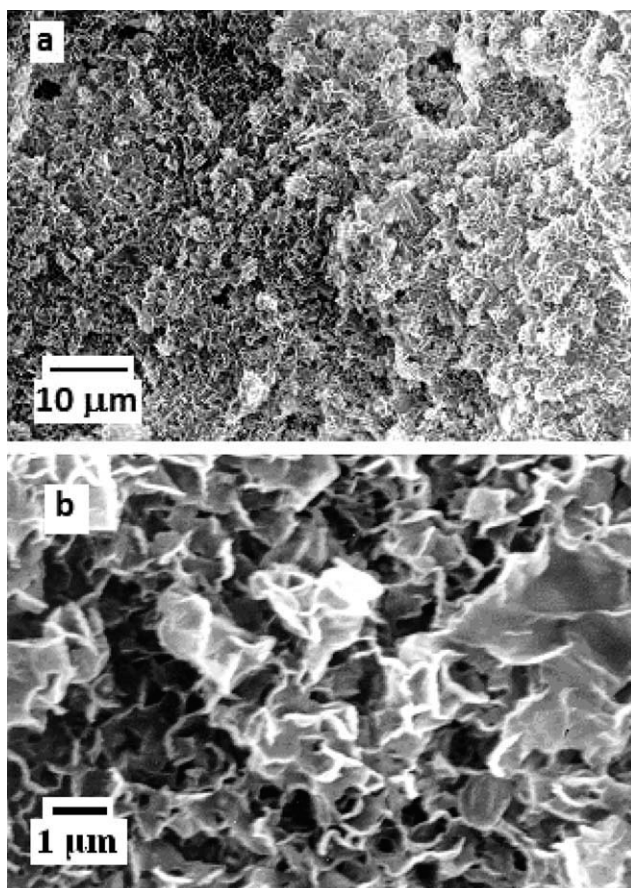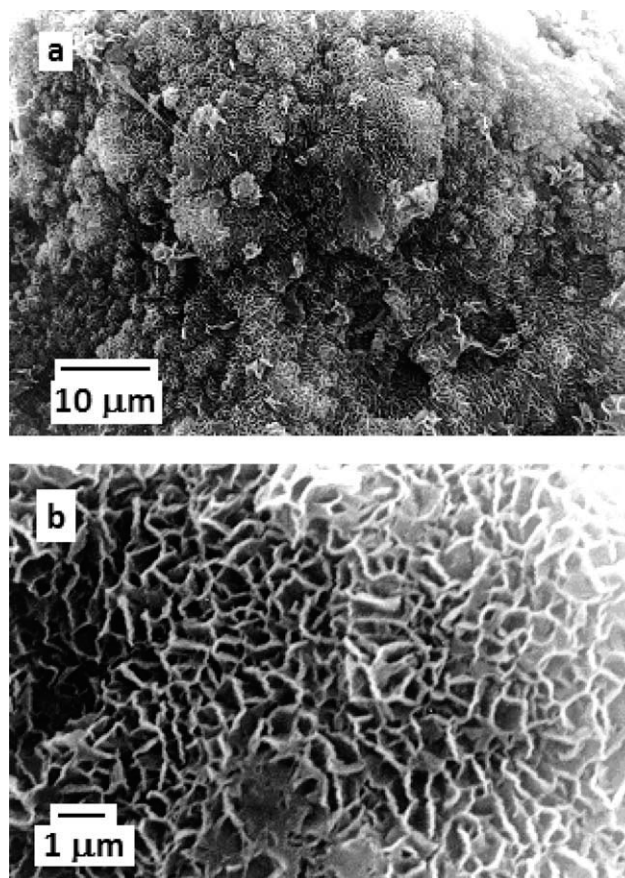
Figure 4. (a) and (b) Morphologies of fractured foam obtained from 38.3% poly(AA)-grafted GUR 412 at two magnifications.

UHMWPE is similar to the pure UHMWPE foam (Figure 1). Poly(NVP) (Figure 3) has also amphiphlic properties which ensure compatibility with the UHMWPE during the production of the foam in the hot gel solution, which results in dimensionally and mechanically strong foams.

The remaining water-soluble homopolymers used in this study; namely, poly(AA) Figure 4 (a,b), poly(MAA), Figure 5 (a,b), and poly(AAm) can do strong hydrogen bonds in themselves. Indeed, these two figures show slightly different morphology compared with Figures 1–3. It seems these foams are more compact than the rest. Furthermore, the possibility of chain scission during irradiation because of the presence of vinylic —CH$_3$ groups in the poly(MAA) may prevent crosslinking, therefore, relatively better stable foams can be expected from the poly(NNDAm), poly(NVP), and poly(AA)-grafted powder of the UHMWPE. But, none of the grafted UHMWPE powders produced stable foams as good as the virgin UHMWPE even though the grafting level was as low as 6%. During the grafting process, the grafting polymers may wrap the UHMWPE powders so tightly that they do not allow the UHMWPE powders to disentangle, swell, and orient freely as they alone formed gel in hot xylene solutions. But, the poly(NNDAm), poly(NVP), and poly(MAA)-grafted UHMWPE powders yielded markedly more stable hot gel solutions, which resulted in better foams consequently.


Figure 5. (a) and (b) Morphologies of fractured foam obtained from 38.3% poly(MMA)-grafted GUR 412 at two magnifications.

To improve the foam structure and property without losing its hydrophilicity substantially, some virgin UHMWPE was added to the grafted powder resin sample in the preparation of hot gel solutions. The stability of the gels and thus the shape and structure of the foams get better as the percentage of the virgin UHMWPE increases. The visual general shape of the foams belonging to [virgin GUR 412], [pure poly(MAA) and
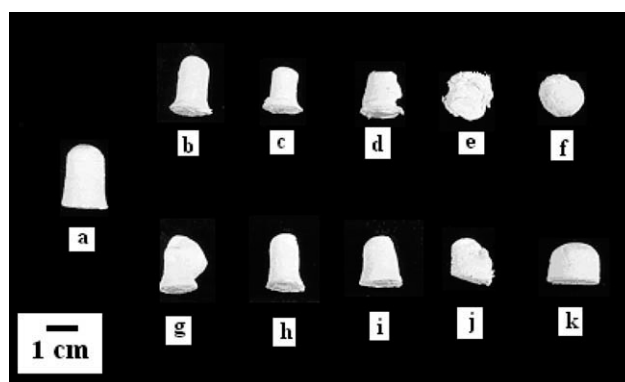
Figure 6. Visual general shape of foam obtained from (a) Pure GUR 412, and (b) 80, (c) 60, (d) 40, (e) 20 and (f) 0% virgin GUR 412 added to 24.7% poly(MAA)-grafted GUR 412, and (g) 80, (h) 60, (i) 40, (j) 20 and (k) 0% virgin GUR 412 added to 37.0% poly(NNDAm)-grafted GUR 412.
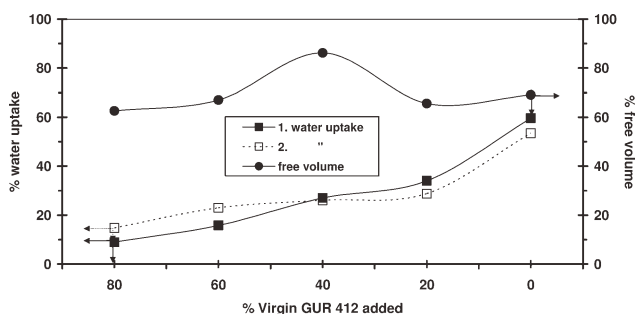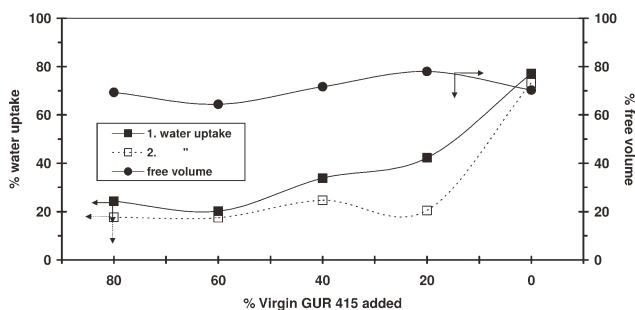
Figure 7. First and second % water uptakes and % free volume of foams obtained from 37% poly(NNDAm)-grafted GUR 412 powder.

Figure 9. First and second % water uptakes and % free volume of foams obtained from 38.3% poly(NVP)-grafted GUR 412 powder.

poly(NNDAm)-grafted GUR 412], and [virgin GUR 412 added grafted powders at various ratios] were given in photographs in Figure 6. The expected shape of the foams should have been the shape of tube which was cylindrical into which the hot gel solutions were poured during foam formation. Stable foam cannot be obtained from the pure poly(AAm)-grafted GUR 412 and also the shapes of the pure poly(AA)-grafted GUR 412 foams were not good, and therefore, they were not given in figures.
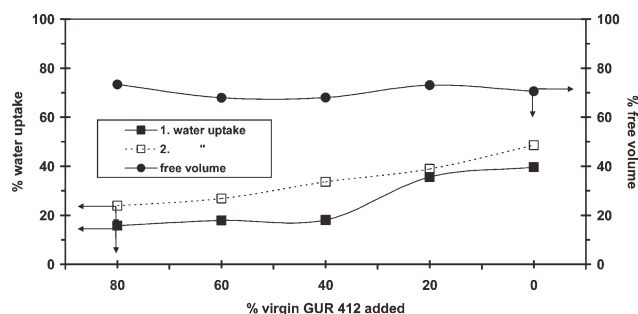
In summary, the foam forming ability of the grafted GUR 412 showed an order of NNDAm > NVP, MAA > AA > AAm with probable relationships with hydrogen bonding and crosslinking properties under irradiation conditions. In addition, greater the grafting on UHWMPE difficulty in making foams becomes substantial because of the weaker interactions between hydrophilic and hydrophobic parts. Secondly, for GUR 415 PE the increased molecular weight results even extra problems of forming gel, hence at higher grafting without addition of virgin GUR 415 no stable foams were obtained.

Free Volume and Water Uptake of Foams
The free volume and water uptake of the foams were given respectively in Figures 7 and 8 for the poly(NNDAm), Figure 9 for the poly(NVP), Figure 10 for the poly(AA), Figure 11 for the poly(MAA), and Figure 12 the poly(AAm)-grafted UHWMPE. Also, the water uptake of the pure UHMWPE foam was found to be as 10%, which is so high compared with the absolutely hydrophobic UHMWPE powder and film. Therefore, this can be regarded as the water trapped in the structure of the foams under forcing conditions which was not enough to permit water to pass through. Furthermore, the water left in the

pure UHMWPE foam easily dried even at room temperature. All of the other foams obtained from the grafted UHMWPE with and without added virgin UHMWPE allowed the passage of water with suction. Water permittivity of these foams indicates their real ability of water absorption. i.e., water can wet the inside surface of the foams and additional water can flow easily through the wetted surface. Thus, suction can prevent the pores to be filled with water.

The water-uptake capacities of the foams are ordered in the following way: NNDAm > NVP > AA > AAm > MAA where the values are significantly greater than 10% except for the poly(MAA)-grafted GUR 412 foam. The similar order was also observed in foam forming abilities of the grafted UHMWPE other than the MAA. However, the poly(MAA) ranks the last, probably due to its low grafting level (24.7%) and its high tendency toward chain scission under radiation which breaks down its three dimensional water uptake structure.

Generally, the grafted GUR 412 foam gave more consistent results than the GUR 415 foams probably due to GUR 415's higher molecular weight, which caused higher molecular entanglement and physical crosslinking during the process. The GUR 412 tolerated the presence of a relatively incompatible material (water soluble polymer) better than the GUR 415 in foam formation.

Although the free volume of the foams did not show very much variation with the addition of virgin powder, which varied between 60–80%, the water-uptake capacities of the foams increased as the amount of virgin powder decreased. The pure grafted UHMWPE, especially poly(NNDAm) grafted ones

Figure 8. First and second % water uptakes and % free volume of foams obtained from 37% poly(NNDAm)-grafted GUR 415 powder.
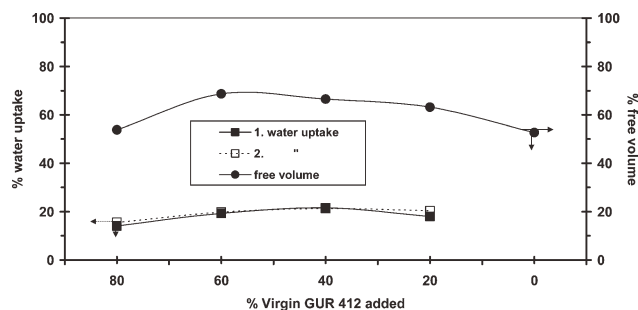

Figure 10. First and second % water uptakes and % free volume of foams obtained from 35.9% poly(AA)-grafted GUR 412 powder.

showed definitely much higher water uptake (50–70%) than any other cases (20%).

This observation of increasing water uptake capacity at constant free volume is the real indication of the presence of hydrogel material grafted in the interior of the foams which absorb water. In general, the water uptake values were usually smaller than the free volume of the foams if the virgin UHMWPE was added, which showed the inhibition of hydrophilicity slightly.

The poly(NNDAm) and poly(NVP)-grafted UHMWPE foams have promising water uptake capacities and free volumes together with their dimensionally stable and strong structures. In the case of the poly(AA) and poly(AAm)-grafted foams, water-uptake remains constant at 15–25%, and some decrease was even observed with the increase in the portion of the grafted UHMWPE. The high molecular weight poly(AA) (5×10^6) is totally insoluble in water, and it shows a hydrophobic behavior in its powder form, because the obtained high molecular weight graft chains of the poly(AA) and poly(AAm) probably results in low water uptake of the foams and crosslinking to a certain extent.[15]

CONCLUSION

Hydrophilic stable macroporous foams water soluble monomer grafted were obtained with uniform porosity ranging from 1–10 μm. Powders of five different water soluble polymers grafted UHMWPE were prepared by precipitation from gel in xylene solution. These foams possessed high mechanical strength, excellent inertness due its PE backbone while they provide an acceptably enough hydrophilic property.

To enhance the mechanical properties of the foams, the pure UHMWPE powders were added to the grafted UHMWPE powder resin at various ratios. An addition of 20% virgin UHMWPE into the grafted powders was enough to obtain stable gel and foam for all of the highly grafted powders. However, the poly(NVP) and especially poly(NNDAm)-grafted UHMWPE powder produced stable foams without adding any virgin UHMWPE. This can be attributed to the compatibility of poly (NNDAm) with UHMWPE due to the impotence of the poly (NNDAm) to hydrogen bonding and crosslinking. However, poly (MMA (methyl methacrylic acid))-grafted UHMWPE even at low grafting created the highest difficulty because of H-bonding.

The SEM photographs showed uniformity of the foams with flake-like structure without any indication of incompatibility or
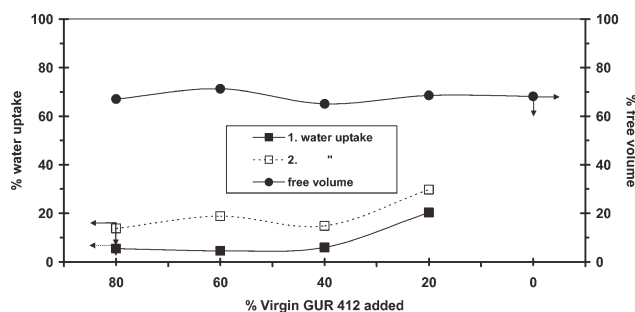
Figure 11. First and second % water uptakes and % free volume of foams obtained from 24.7% poly(MAA)-grafted GUR 412 powder.
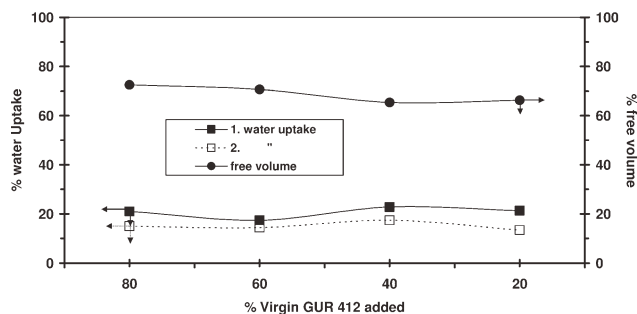
Figure 12. First and second % water uptakes and % free volume of foams obtained from 32% poly(AAm)-grafted GUR 412 powder.

phase separation between the water soluble polymers and PE backbone. Although all SEMs appear to be the same, poly (MMA) and poly(AA) showed compact structures compared with nonH-bonding grafts poly(NVP) and poly(NNDAm).

The water absorbing capacities were found to differ with respect to grafting monomer and added virgin PE to make stable foam. The type of water soluble monomer poly(NVP) and poly (NNDAm) showed higher water absorbing capacities than that of H-bonding making grafting polymers. It seems that H-bonding restricts excessive water into to the foam matrix.

One very important and conclusive remark is that in all cases, the obtained foams keep their dimensional stability and strength even at the highest water presence.

The foams obtained in this study providing acceptably enough water uptake with high dimensional stability and good mechanical properties are promising materials for further applied studies.

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