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Effect of spinning parameters on mechanical strength of polysulfone and polyvinylidene difluoride capillary ultrafiltration membrane

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ABSTRACT

Fiber breakage often limits the life of the ultrafiltration capillary module and calls for the module replacement in an operating installation. Ultimate tensile strength (UTS) of the capillary fiber is thus an important qualifying parameter along with the separation performances and hence development of capillary membranes having enhanced mechanical strength is need of the time. In this paper, the effect of various governing parameters of wet spinning process for making UF capillary membrane fibers namely, polymer casting composition, bore fluid flow rate and drying conditions on ultimate tensile strength of polysulfone and polyvinylidene difluoride capillary membranes have been studied. It was observed that the fiber strength increases with increase in bore fluid flow rate and concentration of drying solution. Addition of surfactant in drying medium has shown decreased fiber strength.

1. Introduction

Advances in membranes have led to significant inroads in the separation technologies in many areas because of flexibility and performance reliability of membrane system, cost competitiveness, increasing demand and environmental awareness as reported by Eykamp W. Ultrafiltration (UF) is one of the pressure driven membrane process having wide industrial applications. One such application is pretreatment of seawater in place of conventional pretreatment system. UF process offers advantages such in being modular system, ease of operation and is a robust alternative to conventional treatments which is known to be complex, labour intensive and requiring larger footprint area as reported by Voutchkov N. UF membrane in capillary configuration has high packing density is amenable for easy backwash, causes lower pressure drop, etc. Polysulfone (PSf) and polyvinylidene difluoride (PVDF) are widely used polymer materials for preparation of capillary UF membrane as described by

Mamtani V. S. *et al.* The advantages of these polymers are that the PSf has high mechanical strength, good thermal and chemical resistance while PVDF is a specialty thermoplastic fluoropolymer having outstanding oxidative, thermal and hydrolytic stability.

During application of UF capillary membranes, fiber failure has been reported with an annual fiber failure rate in between 1 to 10 per million fibers as reported by Gijsbertsen-Abrahamse A. J. et al. Fiber failure causes leakage of feed water to the permeate side of the membrane resulting in deteriorating the quality of the permeate. Failure of fiber can be caused by chemical attack, faulty installation, presence of foreign bodies or poor membrane strength. Prediction of fiber failure due to chemical attack, faulty installation and due to presence of foreign body can be identified and corrective actions can be taken either by replacement of membrane material compatible to chemicals present in the feed, by proper installation of membrane & module, and by proper treatment of feed before sending it to UF membrane module. However, Childress Amy E. *et al.* reported the failure of fiber resulting from an external load applied under normal operating conditions, necessitates consideration of the development of the membrane fiber with sufficient strength to withstand the required operating pressure condition. Mechanical properties especially, tensile strength is very important parameter to be considered for capillary membrane fibers as they are self-supporting. When a high pressure is applied to a fiber with a low ultimate tensile strength (UTS), the fiber may break whereas a fiber with high UTS can easily withstand higher pressures.

Normally capillary membranes are prepared by wet spinning phase separation process wherein a polymer dissolved in appropriate solvent along with suitable additives is used. The final tensile strength of the fiber is affected by various capillary membrane preparation process parameters namely polymer concentration, type of polymer chosen, bore fluid flow rate, fiber spinning rate [Qin Jianjun *et al.*] drying methodology, etc. During the preparation membrane symmetry or asymmetry is decided which plays a significant role in the strength of the final fiber. Further, fiber diameter and wall thickness which contributes to strength of the fibers is also dependent to a lesser extent on the preparation process parameters. As very large formulation space exists for making capillary membrane using PSf or PVDF polymers, there is wide flexibility in preparing the membrane for a particular application with sufficient tensile strength. The objective of this work is to study systematically the effect of polymer concentration, type of polymer chosen, bore

fluid flow rate, drying methodology on the final strength of the PSf and PVDF capillary fiber. More details study is focused on PVDF polymer which has comparatively lower strength inherently than the PSf polymer.

2. Experimental

2.1 Materials

Polysulfone (Av. molecular weight: ~50-60KDa, Solvey India make), polyvinylidene difluoride (Av. molecular weight: ~300KDa, Solvay Solef make), N-methyl pyrrolidone (NMP; 99.0% pure, Sigma-Aldrich make), polyvinylpyrrolidone (PVP, Molecular Weight: 40KDa, Sisco Research Laboratory make), glycerol (Sisco Research Laboratory make) and surfactant 'sodium lauryl ether sulfate (Sisco Research Laboratory make)' were used as such without further purification.

Table 1. Compositions of PVDF/PSf dope solution

Components of dope solution	Compositions (wt. %)			
Polymer	17.86 (PSf)	15.7 (PVDF)	17.2 (PVDF)	17.86 (PVDF)
PVP	12.6	12.6	13.8	12.6
NMP	69.54	71.7	69.0	69.54

2.2 Process Set-up and Membrane Preparation

The dope solutions were prepared using either PSf or PVDF homopolymer along with PVP and NMP at different compositions given in Table 1. The dope solution was pressurized under nitrogen pressure of 1 bar above atmospheric pressure along the annular gap in the spinneret. The bore fluid (UF treated service water) was pumped through the axial bore of spinneret using peristaltic metering pump. The polymer dope solution and the non-solvent 'water' are contacted at the outlet of spinneret (O.D = 2 mm and I.D = 1 mm; Fig. 2) causing phase inversion and capillary membrane formation. As depicted in Fig.1, the nascent capillary fiber coming out from the spinneret is passed into water bath (external coagulant) where solvent is replaced by water. During the membrane preparation, dope solution is kept at ambient temperature in the range of 24-26°C; humidity was in the range 45-51%; bore fluid and external coagulant were deionized water. The air gap between spinneret and external coagulant bath was maintained in the range of 100-120 mms. Further, the water bath (about 200 litres) was drained and replenished each day for 4 days after which capillary membrane fibers were dried with glycerol at different compositions (2-10 vol. %). In few experiments, washing with surfactant sodium lauryl sulfate (0.2 %) was used before drying with glycerol (10 vol. %).

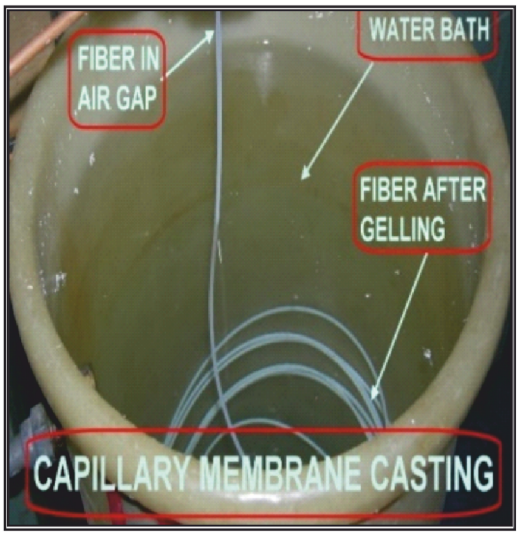

Fig. 1 Spinning of capillary membrane

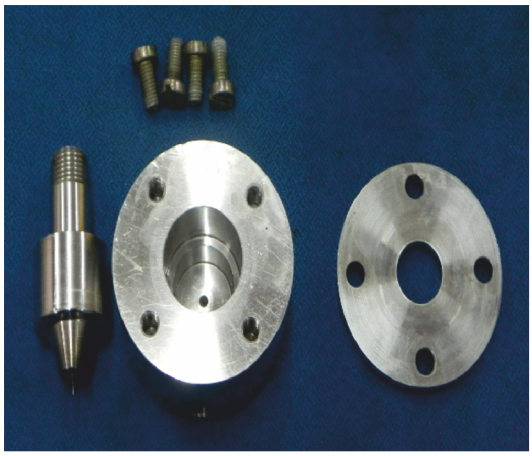

Fig. 2 Dismantled spinneret

Fig. 3 Universal Testing Machine (UTM)

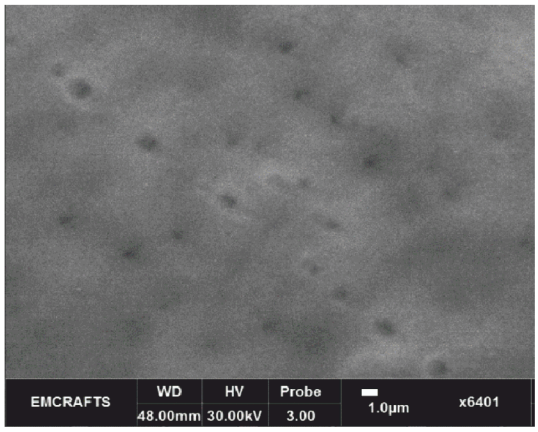

Fig. 4 SEM image of outer surface of PSf capillary membrane

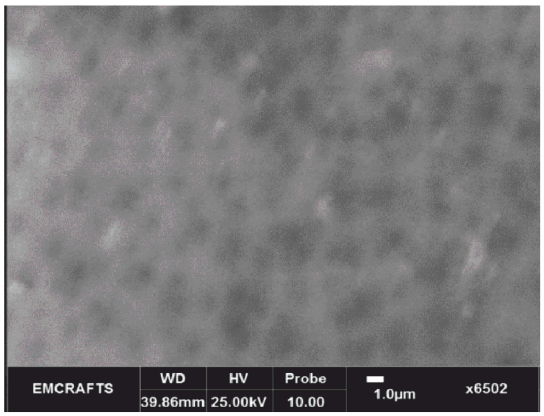

Fig. 5 SEM image of outer surface of PVDF capillary membrane

2.3 Capillary Membrane fiber testing

Fibers of capillary membrane were tested with Universal Testing Machine (UTM) [make: HEMETEK LRX plus, Llyod Instruments] for its Tensile strength as shown in Fig. 3. The testing was done by keeping clamp distance of 120mm & extension rate of 50mm/min at 22-25°C. The outer surfaces of capillary membrane were inspected using Scanning Electronic Microscopy (SEM) [make: EMCRAFTS, Cube 100]. SEM samples of the membranes were prepared by coating the membrane with Gold using Ion Coater (EMCRAFTS).

3. Results and Discussion

The outer surfaces of PSf and PVDF capillary membranes were inspected using SEM as shown in Fig. 4 & Fig. 5. The images shows that both the membranes do not have any surface defects and PSf capillary membrane has more porosity than PVDF membrane. The approximate pore diameter for both the membranes is in the range of 0.5 to 2 µm.

The fibers were further tested with UTM. The effects of nature of the polymer, composition of polymer in dope solution, bore fluid flow rate and different drying conditions on the strength of the fiber were studied by obtaining the final UTS values of the fiber and the Stress vs. Strain curve for each fiber. The results are described and discussed in the following sections.

3.1. Effect of polymer (PSf and PVDF) in dope on UTS of the final capillary membrane fiber

The PSf and PVDF capillary membrane fibers prepared under the same polymer dope composition pressurized by Nitrogen gas at 2 bar and under same bore fluid rate (8ml/min) with drying condition of 10 % glycerol without washing with surfactant were tested for finding UTS. As can be seen from Table 2, the UTS of PSf (2.7 MPa) is more compared to UTS of PVDF (1.25 MPA). The typical Stress vs. Strain relationship obtained for PSf and PVDF fibers are shown in Fig.6 and Fig.7 respectively. The stress and the strain that PSf capillary membrane fiber can sustain are much higher than that from PVDF. The curves obtained are in relation to the strength of pure polymer [higher for PSf (69 MPa) than that of PVDF (43 MPa)] as reported by Mamtani V. S. *et al*.

Table 2. Ultimate Tensile Strength for capillary fibers membrane made from different polymers (PSf and PVDF)

Sl. No.	Name of the parameter	PSf	PVDF
1	PVDF, (wt. %)	17.86	17.86
2	PVP, (wt. %)	12.6	12.6
3	NMP, (wt. %)	69.54	69.54
4	Drying (Glycerol vol.% for 24 hours)	10	10
5	Bore fluid flow rate, (ml/min)	8	8
6	Tensile Strength, (MPa)	2.7	1.25

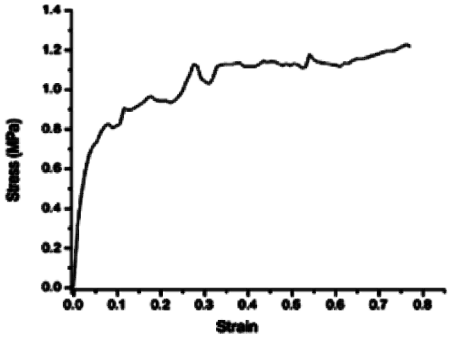

Fig.6. Stress vs. Strain for PSf capillary membrane fiber (17.86 wt. % of PSf in dope)

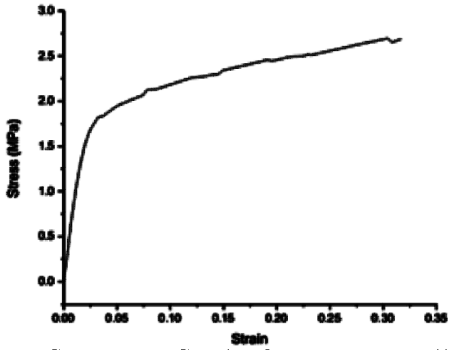

Fig.7. Stress vs. Strain for PVDF capillary membrane fiber (17.86 wt. % of PVDF in dope)

3.2. Effect of polymer composition (PVDF) in dope solution on UTS of the final capillary membrane fiber

PVDF capillary membrane fibers prepared under different polymer dope composition pressurized by Nitrogen gas at 2 bar and under same bore fluid rate (8ml/min) with drying condition of 10 % glycerol without washing with surfactant were tested for finding UTS. As can be seen from Table 3 that the UTS of fiber increases with increase in polymer concentration in the dope solution. The typical Stress vs. Strain relationship obtained for PVDF fibers with different composition of PVDF in dope viz. 15.7 wt. %, 17.2 wt. % and 17.86 wt. % are shown in Fig.8, Fig.9 and Fig.7 respectively. The reason for increased strength in fiber can be attributed to increased packing of the polymers and reduction of the porosity. It can also be noted that the strength increases with polymer composition significantly initially however further increase in polymer composition increases strength slightly. Also increase in PVDF composition more than 18 wt. % in NMP dope solution results in polymer chunk formation which cannot be used for spinning capillary membrane. Hence, to obtain higher strength, the polymer composition for PVDF in the NMP dope can be restricted in the range of 17-18 wt.%.

Table 3. Ultimate Tensile Strength for PVDF

capillary membrane fibers made at different polymer composition

Sl. No.	Name of the parameter	Batch 1	Batch 2	Batch 3
1	PVDF, (wt. %)	15.7	17.2	17.86
2	PVP, (wt. %)	12.6	13.8	12.6
3	NMP, (wt. %)	71.7	69.0	69.54
4	Tensile Strength, (MPa)	0.85	1.20	1.25

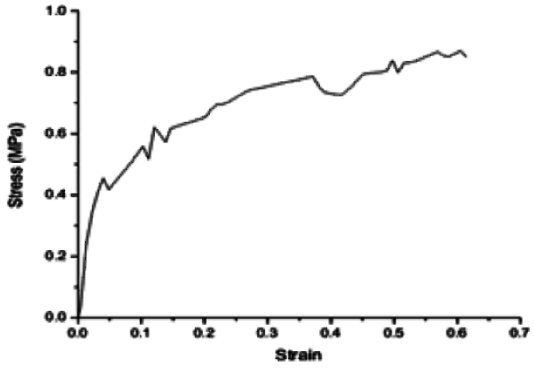

Fig.8. Stress vs. Strain for PVDF capillary membrane fiber with 15.7 wt. % of PVDF in dope and bore fluid flow rate of 8 ml/min

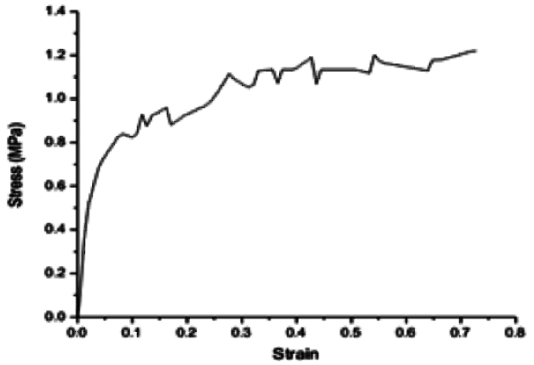

Fig.9. Stress vs. Strain for PVDF capillary membrane fiber with 17.2 wt. % of PSf in dope and bore fluid flow rate of 8 ml/min

Table 4. Ultimate Tensile Strength for PVDF capillary membrane fibers made at different bore fluid flow rate

Sl. No.	Name of the parameter	Batch 1	Batch 2	Batch 3
1	PVDF, (wt. %)	17.2	17.2	17.2
2	PVP, (wt. %)	13.8	13.8	13.8
3	NMP, (wt. %)	69.0	69.0	69.0
4	Drying (Glycerol vol.% for 24 hours)	10	10	10
4	Bore fluid flow rate, (ml/min)	6	8	10
5	Tensile Strength, (MPa)	1.10	1.20	1.23

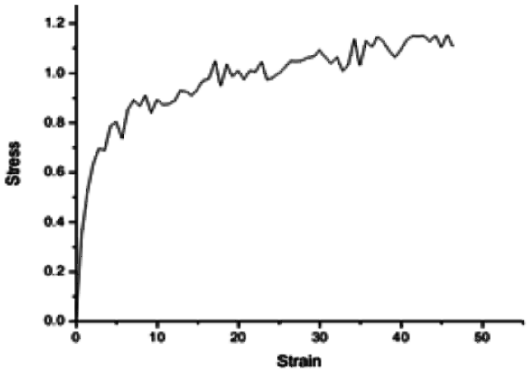

Fig.10. Stress vs. Strain for PVDF capillary membrane fiber with 17.2 wt. % of PVDF in dope and bore fluid flow rate of 6 ml/min

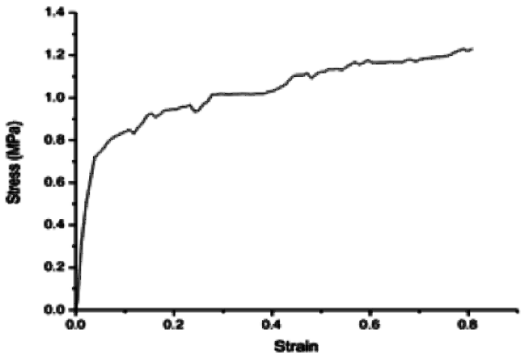

Fig.11. Stress vs. Strain for PVDF capillary membrane fiber with 17.2 wt. % of PVDF in dope and bore fluid flow rate of 10 ml/min

3.3. Effect of bore fluid flow rate on UTS of the final capillary membrane fiber

The PVDF capillary membrane fibers prepared under same polymer dope composition pressurized by Nitrogen gas at 2 bar with different bore fluid rate (6ml/min, 8ml/min and 10 ml/min) under same drying condition of 10 % glycerol without washing with surfactant were tested for finding UTS. The UTS data for PVDF capillary membrane fibers made at different bore fluid flow rate is given in Table 4. It can be seen that the UTS of fiber increases with increase in bore fluid flow rate. The typical Stress vs. Strain relationship obtained for PVDF fibers with different bore fluid flow rate viz. 6ml/min, 8 ml/min and 10 ml/min respectively are given in Fig.10, Fig. 9 and Fig.11 respectively. The reason for increased strength in fiber can be attributed to increased solvent removal rate by bore liquid at higher bore fluid flow rate and hence reducing the pore size of the capillary membrane fiber. It is also be noted further that similar to polymer composition, the increase in bore fluid flow rate from 6ml/min. to 8ml/min. increases the strength significantly but from 8ml/min to 10 ml/min., strength of the fiber increases slightly. The higher bore fluid flow rate is desirable for obtaining higher fiber strength, however the performance of the membrane is also to be considered while fixing the bore fluid flow rate as it can significant effect the pore size of the membrane and thus change the separation characteristics.

Table 5. Ultimate Tensile Strength for PVDF capillary membrane fibers made with different drying conditions

Sl. no.	Name of the parameter	Batch 1	Batch 2	Batch 3	Batch 4
1	PVDF, (wt. %)	17.2	17.2	17.2	17.2
2	PVP, (wt. %)	13.8	13.8	13.8	13.8
3	NMP, (wt. %)	69.0	69.0	69.0	69.0
4	Bore fluid flow rate, (ml/min)	8	8	8	8
5	Surfactant wash vol.% + Drying (Glycerol vol.% + water for 24 hours)	Yes (0.2% surfactant washing); 10% glycerol+ 90% water	No; 2% glycerol+ 98% water	No; 6% glycerol+ 94% water	No; 10% glycerol+ 90% water
6	Tensile Strength, (MPa)	0.93	1.05	1.1	1.20

3.4. Effect of drying methodology and surfactant washing on UTS of the final capillary membrane fiber

The PVDF capillary membrane fibers prepared under same polymer dope composition pressurized by Nitrogen gas at 2 bar with same bore fluid rate (8ml/min) under different drying conditions of (2%, 4%, 10%) with or without washing with surfactant which were further tested for finding UTS. As can be seen from Table 5 that the UTS of fiber increases with increase in glycerol concentration in drying solution. Hence, a higher glycerol content (10 vol.% or more for PVDF membrane prepared using NMP) in drying solution is desirable so that water inside fibers is replaced by glycerol and pores do not collapse when the fiber is dried. It was also be noted that the washing of fiber with surfactant (sodium lauryl sulfate at 0.2 vol. %) decreased the strength of the fiber significantly as further drying with 10% glycerol solution also could not improve the strength. However, visible smoothness was seen in the fibers having surfactant wash before drying while those fibers without surfactant washing were little rough by visual observation. The typical Stress vs. Strain relationship obtained for PVDF fibers with different drying conditions are shown in Fig.12, Fig.13, Fig.14 and Fig.15 respectively. The reason for increased strength in fiber with increase in glycerol composition in drying solution can be attributed to higher deposition of glycerol in the pores and thus preventing the pore collapse and hence increasing the strength of the fiber.

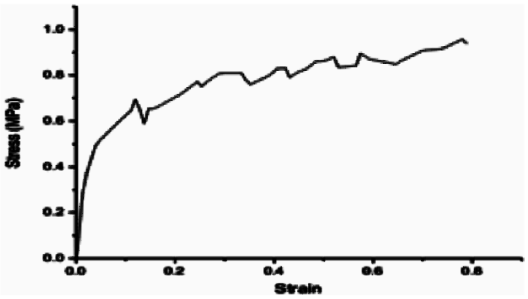

Fig.12. Stress vs. Strain for PVDF capillary membrane fiber with drying condition of 0.2 vol. % sodium lauryl sulfate surfactant washing followed by glycerol (10 vol. %) solution drying

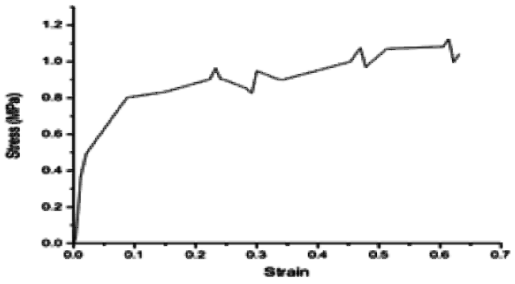

Fig.13. Stress vs. Strain for PVDF capillary membrane fiber with drying condition of no surfactant washing and by glycerol (2 vol. %) solution drying

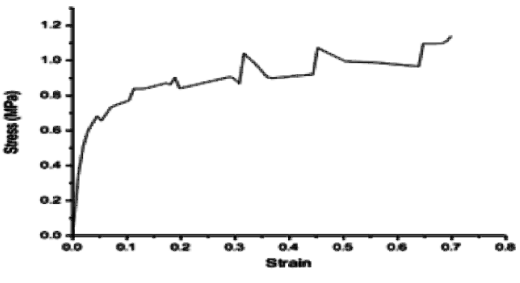

Fig.14. Stress vs. Strain for PVDF capillary membrane fiber with drying condition of no

surfactant washing and by glycerol (6 vol. %) solution drying

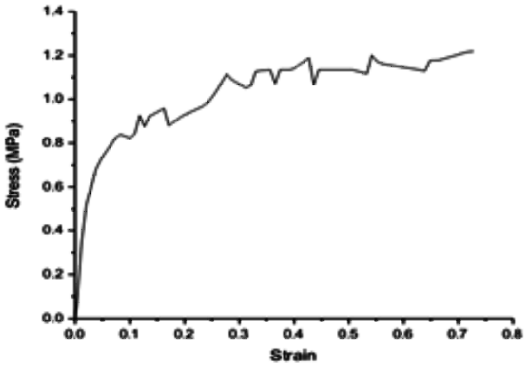

Fig.15. Stress vs. Strain for PVDF capillary membrane fiber with drying condition of no surfactant washing and by glycerol (10 vol. %) solution drying

4. Conclusions

The strength of capillary membrane fiber is strongly related to the polymer used, the composition of the polymer in dope solution, bore fluid flow rate and drying condition among other parameters. The UTS for PSf capillary membrane fiber is higher as compared to PVDF. The increase in concentration of the polymer in casting dope solution increases the strength significantly initially and then later slightly in lower rate. The PVDF polymer concentration in the NMP dope should be in the range of 17-18 wt.% for having good mechanical strength of the fiber without sacrificing separation performance properties. Increase in bore fluid flow rate increases strength of the fiber significantly initially and later slightly but it can also change the separation characteristics of the membrane significantly. Optimum bore fluid flow rate should be decided based on the desired strength of the fiber and its desired separation characteristics. The increase in glycerol concentration in drying solution increases the strength of the fiber and accordingly higher glycerol content in drying solution is desirable but it should be related to overall pore volume of capillary membrane fibers. The surfactant washing before drying significantly decreases the strength.

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