

4.1 Introduction

An ideal clothing fabric, in terms of thermal comfort, should have the following attributes: (1) high thermal resistance for protection from the cold; (2) low water vapour resistance for efficient heat transfer under a mild thermal stress conditions; and (3) rapid liquid transport characteristics for transferring heat efficiently and eliminating unpleasant tactile sensations due to perspiration under high thermal stress conditions.

Extremely cold weather protective clothing refers to garments that are used in extreme climates such as on the Trans-Antarctica expeditions, in skiwear, mountaineering and for army personnel posted in hilly areas at high altitudes. For this purpose, clothing that provides a high degree of insulation with the least amount of bulk is most desirable. For such applications, breathable membranes and coatings, and high-loft battings of special fibres in conjunction with reflective materials have been suggested.¹⁻³

For the International Trans-Antarctica Expedition in 1990, the outerwear was made with Gore-Tex fabric constructed of a highly porous membrane bonded to a high performance textile. This outerwear was found to be completely windproof and waterproof, yet 'breathable' to allow the body's perspiration vapour to escape. To encounter the harshest weather in the Antarctic region, where winds can reach 150 miles per hour during storms and temperatures fall to -46°C , a layered clothing system has been developed to enable the wearer to continually adjust his clothing to conserve and manage his body heat. The protection of an individual in a cold environment would depend on the following main factors: (1) metabolic heat, (2) wind chill, (3) thermal insulation, (4) air permeability and (5) moisture vapour transmission. Survival depends on the balance of heat losses due to (2)–(5) and heat output due to metabolic heat (1).

US Army Research Institute of Environmental Medicine (USARIEM) studies⁴ have examined the effects of temperature and wind chill on a human body and indicated that the sensations of warmth and cold at wind velocities between 2 to 32 m/s may be as below:

32 °C	Hot
28 °C	Pleasant
22 °C	Cool
16 °C	Very cool
10 °C	Cold
5 °C	Very cold
0 °C	Bitterly cold
– 5 °C	Exposed flesh freezes
– 24 °C	Exposed area of face freezes within one minute
– 32 °C	Exposed area of face freezes within $\frac{1}{2}$ minute

Wind chill depends on the temperature as well as velocity of the wind. In cold climates, consideration of the wind chill effect is very important, because 80% of heat losses are due to wind chill.

Wind chill factor can be derived from the Siple Passel formula (source: Slater K, *J. Text. Inst.* 1986 **77**(3) 157–171):

$$H = (10.45 + \sqrt{V - V_0})(33 - T_A) \quad [4.1]$$

where

H = heat loss from the body in kcal/m²/h,

V = wind velocity in m/s, and

T_A = air temperature in °C

The skin temperature under calm conditions is taken as 33 °C. The significance of the wind chill factor may be understood by reviewing its effect on the freezing time of exposed flesh. At a wind chill factor of 1000, an individual would feel very cold and at 1200, bitterly cold. When the wind chill factor is 1400, the exposed flesh would freeze in 20 min, at a wind chill factor of 1800, the exposed flesh would freeze in 10 min, and when the wind chill factor is 2400, exposed flesh freezes in 1 min only.

It is evident from Table 4.1 that textile fibres are much better conductors of heat than air (i.e. bad insulators). Therefore, the ideal insulator would be still air. However, there should be some means to entrap the air. Fibrous materials serve this purpose effectively as they have the capacity to entrap huge volumes of air because of their high bulk. For example, a suiting fabric is 25% fibre and 75% air; a blanket is 10% fibre and 90% air; a fur coat is 5% fibre and 95% air. In other words, a textile-based thermal insulator should be capable of entrapping maximum amount of air. The contribution of the fibre itself to thermal insulation comes second. The contribution of convection can be reduced by optimizing the interfibre space. The heat loss due to radiation is not significant. In clothing for extreme cold regions, it is further reduced by incorporating a thin layer of metal-coated film.

Table 4.1 Thermal conductivity of pads of fibres with a packing density of 0.5 m/cc

Fibre	Thermal conductivity (mW/m K)
Cotton	71
Wool	54
Silk	50
PVC	160
Cellulose acetate	230
Nylon	250
Polyester	140
Polyethylene	340
Polypropylene	120
Air (still)	25

Source: Physical Properties of Textile Fibres, Morton W E and Hearle J W S, Third edition, Textile Inst., Manchester, UK, 1993, p. 590.

In this chapter, a brief account of polymers, ceramics, phase change materials as melt additives, breathable coatings and design of fabric assembly for thermal insulation is given.

4.2 Thermal storage and thermal insulating fibres

4.2.1 Use of ceramics as melt dope additives

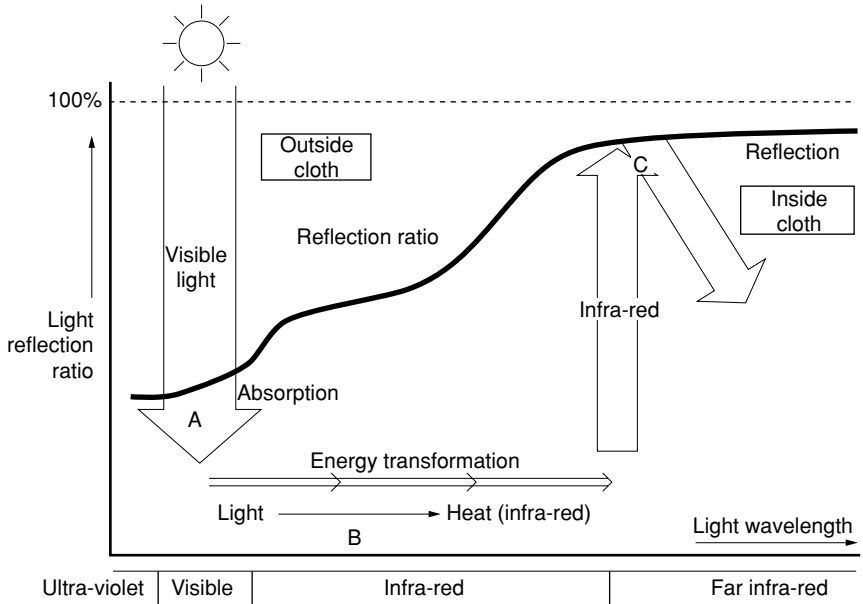
Zirconium, magnesium oxide or iron oxide can be used as particulate fillers in the molten polymer for producing heat generating polyester, polyamide, polyethylene, polypropylene and other functional fibres.

By applying the heat insulation principle, heat-regenerating fibres produced from ceramic composites utilize the far infra-red radiation effect of ceramics, which heat the substrate homogeneously by activating molecular motion. For example, zirconium, magnesium or iron oxide, when blended into manufactured fibres, radiate *ca.* 60 mW far infra-red of wavelengths 8–14 μm at a body temperature of 36 °C. Such fibres have been found suitable for sportswear and winter goods, particularly for those working in extremely cold regions.

There are two possible ways to insulate heat:

- 1 By using a passive insulating material which encloses the body heat
- 2 By use of an active material as an additive or coating that absorbs heat from outside.

The far infra-red radiation ceramics activated by body heat belong to the first category of insulating materials.



4.1 Heat absorption and insulation of Solar- α (Descente).

The active insulating materials which fall in the second category are those electrically heated materials where the electrical energy of a battery is transformed into heat energy by the heater, with this heat supplied by the heat from the oxidation of iron powder. In another system,⁵ the conductive particulate is selected from SnO_2 , BaSO_4 , K titanate and TiO_2 , and the far-IR particulate from one or more of ZrO_2 , Al_2O_3 , TiO_2 , Kaolin and MgO for producing thermal storage and thermal insulating fibres.

Zirconium carbide compounds have been used for their excellent characteristics in absorbing and storing heat in a new type of solar system, including domestic water heaters and large-scale generators. Zirconium carbide reflects the light of long wavelengths over $2\ \mu\text{m}$, but absorbs the light energy of rather short wavelengths ($< 2\ \mu\text{m}$), which make up 95% of sunlight, and converts it into stored heat energy. Descente researchers⁶ used this property of zirconium carbide to achieve 'active insulation', by enclosing microparticles of zirconium carbide in polyamide or polyester fibres. They developed the technology to encapsulate zirconium carbide powder within the core of synthetic fibres, in cooperation with Unitika. The clothes made of this fibre, Solar- α (Fig. 4.1) absorb solar visible radiations efficiently and convert them into heat in the form of infra-red radiation which is released in the clothing. The released heat and the heat radiated from the body are reflected by Solar- α and will not escape from the inside to the outside of clothing.

Unitika⁷ has also disclosed the manufacture of self-stretchable heat-retentive polyester yarns containing Group IV transition metal carbides. Thus, a blend of 95 parts PET and five parts Zr carbide was melt-spun at 3100 m/min and heat-treated at non contacting-type heater temperature 425 °C to give self-stretchable yarn (B) exhibiting stretch at 185 °C of 4.5% and conventionally spun PET fibres drawn at non contacting heater temperature of 285 °C to give yarn (A) having dry heat shrinkage of 4.5%. Interlacing yarns A and B and subsequent twisting produced woven fabric which exhibited surface temperature 21.1 °C initially, 24.5 °C on exposure of fabric to a source of 100 W for 10 min, and 23.2 °C on storing the fabric for 5 min after exposure to light for 10 min.

Mitsubishi Rayon Co.⁸ has reported the development of heat-storage and electrically conductive acrylic fibres with electrical conductivity $> 10^{-6}$ S/cm and clothes for winter clothing and sportswear. These bicomponent fibres comprise a core-sheath structure, a core of P(AN/MA/Sod. methallyl sulphate) containing 15–70 vol % white electrical conductive ceramic particles (e.g. W-P) and P (acrylonitrile/vinyl acetate) as a sheath.

Toyo Kogyo Co.⁹ disclosed the production of insulative antistatic polyester fibres. A blend of PET and 20% pellets comprising 4:1 (wt. ratio) mixture of ceramic powder containing 70 parts Sb_2O_5 and 30 parts SnO_2 (particle size $< 1 \mu\text{m}$) and one part adipic acid-butylene glycol polymer was melt-spun and drawn. A unit of this fibre showed surface temperature of 53.5 °C after exposure to light (300 W) for 60 s and surface resistivity $3.0 \times 10^9 \Omega$ vs. 46.5 °C and $5.2 \times 10^{12} \Omega$, respectively for fibres containing no ceramic powder.

Kuraray¹⁰ claimed the formation of PET fibres with heat-storing/heat insulating properties. Such fibres contain heat-storing agents obtained by impregnating porous materials with organic compounds having melting point 10–50 °C, heat of melting ≥ 20 mJ/mg and crystallization temperature 10–45 °C. Thus, a composition containing PET and decanoic acid-impregnated SiO_2 support was spun to give fibres with heat evolution of 40 mJ/mg.

Insulative fibres with improved heat retention properties have been made by Unitika.¹¹ A melt-kneaded mixture of calcium laurate treated six parts α -alumina (A 50N) with average particle size of 1.0 μm ; four parts of Zr carbide were blended with 90 parts of PET as the core, and PET as the sheath were together melt-spun to give fibres showing a surface temperature of 26.9 °C on exposure to a white light source (100 W) at 20 °C and 65% relative humidity and heat conductivity 29 W/cm °C.

In another patent, production of thermally insulative fabrics from fibres¹² comprising 98 parts nylon 6 and two parts Na stearate-treated α -type Al_2O_3 (AKP-30) particles with average particle diameter 0.4 μm has been disclosed. The mixture was melt spun at 250 °C, drawn, heat-treated at 165 °C, and made into a woven fabric with heat conductivity 2.4×10^{-4} W/cm °C.

Heat-ray-radiating fibres¹³ with high warming and heat insulating properties

have been produced. The fibres, useful for clothes, bed clothes, etc., contain n-type semiconductors showing volume resistivity 30–500 Ω cm. Thus, a non-woven fabric was manufactured from multifilament yarns comprising PET and 3% Al-doped electrical conductive ZnO powder.

Thermally insulative undergarments from blends of metal containing spandex and other fibres have been produced. A blend containing 15% spandex fibres having alumina, silica, titania and Pt at 10:82:3:5 wt. ratio, and 85% cotton showed heat conductivity 4.906×10^{-4} W/cm $^{\circ}$ C and heat retention 28.6%. A ladies' stocking of a blend¹⁴ comprising 6.4% spandex fibres containing alumina, silica, titania and Pt at 10:82:3:5 wt. ratio, 24.1% acrylic fibres and 13.5% nylon fibres also showed heat conductivity 3.525×10^{-4} W/cm $^{\circ}$ C and heat retention 42.3%.

Kuraray¹⁵ has also produced heat storing fibres which contain 0.5–40% mixtures of Group VIII transition metal oxide and TiO₂ at 1/(0.3–2.0 ratio). Thus, Septon KL 2002 (hydrogenated isoprene–styrene triblock rubber) containing 15% powder Fe₃O₄ and 15% powder TiO₂ as the core and PET as the sheath were spun at core/sheath = 1/3, stretched, and heat-set to give multifilaments (75 denier/24 filaments), which were plain-woven, scoured, dyed in black and irradiated with a reflector lamp for 40 s at inside temperature 20 $^{\circ}$ C (inside temperature is the temperature of air between the specimen and a heat insulator in a test apparatus). The fabric showed surface temperature of 54.8 $^{\circ}$ C and inside temperature 33.0 $^{\circ}$ C immediately after the irradiation, and 22.0 $^{\circ}$ C and 25.3 $^{\circ}$ C, respectively, 5 min after the irradiation.

Shimizu¹⁶ has demonstrated the use of substances containing high amounts of H₂O of crystallization, e.g. powdered borax, Al(OH)₃, Zn borate, Ca(OH)₂ or powdered alum as fillers for producing self-extinguishing far-IR radiating heat insulative fibres. A blend comprising 100 parts master batch containing PET and 30% Al(OH)₃ and 500 parts PET was pelletized and spun to give self-extinguishing fibres containing 5% Al(OH)₃.

4.2.2 Hollow fibres

Use of hollow fibres in place of cylindrical fibres affects the physical properties of the product. A reduced heat transfer is of special interest under the changed physical properties for fibre-filled products such as pillows, mattresses, sleeping bags, etc. In such products, synthetic hollow fibres have been given preference for many years.¹⁷

Kawabata¹⁸ also used an empirical approach to show that the thermal conductivity of single fibres along their axis is about ten times as great as heat conductivity in a direction transverse to the fibre axis. This thermal anisotropy and its implications on the effects of fibre orientation within the web become especially interesting when considering the hollow fibres now often used in insulation batts.

Lightweight hollow fibre thermally insulating fabrics for winter clothing have been produced by Unitika.¹⁹ A composition containing 98 parts nylon 6 and two parts sodium stearate treated- α - Al_2O_3 particles (AKP-30) was melt-spun to form fibres with degree of hollowness 30%, drawn and made into woven fabric exhibiting heat transmission $1.6 \times 10^{-4} \text{ W/cm } ^\circ\text{C}$.

Nylon fibres²⁰ having a hollow, square-shaped cross-section (A) with two perpendicular protrusions (B) at each end for insulative garments are produced as follows: A composition containing 96 parts nylon 6 and four parts zirconium carbide as the (A) section-forming component and nylon 6 only as the (B) portion-forming component were melt-spun together at 275°C to give hollow non-circular fibres with heat retention temperature by a specified test as 26.1°C .

Hollow insulative lightweight polyester fibres have also been produced by Toray Industries.²¹ The fibres have a circular cross-section with a triangular hollow portion having a specified dimension. A polyester was melt-spun through a spinneret with each hole comprising three arc-shaped slits, cooled by blowing air onto the fibres, lubricated, and drawn to give fibres with degree of hollowness 20.2% and lustre 98.5%.

Hollow hygroscopic insulative PET fibres with good pilling resistance²² have been produced. A composition comprising 100 parts ethylene glycol-sodium 5-sulfoisophthalate-terephthalic acid copolymer (I) and three parts polyethylene glycol as the core, and PET as the sheath were together melt-spun at 50:50 ratio, made into a woven fabric and subsequently treated with an alkali solution to dissolve I and give a lightweight insulative fabric with water absorption 146 mm and good pilling resistance.

Heat-insulative hollow PET fibres with pores extending from the surface of the fibres to the hollow portion of the fibres and with the hollow portion containing slowly releasable hygroscopic polymer gels have been disclosed by Teijin.²³ The fibres are useful for undergarments and gloves. Poly(ethylene terephthalate) was melt-spun through a spinneret and drawn to form hollow fibres with degree of hollowness 40%. They were made into a tricot, then treated with NaOH solution to cause weight loss of 20% to give fibres having ≥ 1 pore with width $0.2\text{--}2.0 \mu\text{m}$ and length $10\text{--}15 \mu\text{m}$ per $100 \mu\text{m}$. In another system, the knit was immersed in an aqueous solution containing Na acrylate 20, acrylic acid 5, and polyethylene glycol dimethacrylate 10 parts in a container for 10 min at 0.2 torr, subsequently immersed in H_2O for 3 min at 100°C , dried and heat-treated for 1 min at 120°C to give a knit with weight increase 23.5% and exhibiting moisture absorption 15.0% and average body temperature retention rating (5 best, 1 worst) 4.5 by a specified test.

Porous insulative polypropylene fibres²⁴ have been produced by melt-spinning of polypropylene (I) with melt index (MI) 0.8, heat-treated at 150°C for 24 h, and drawn to give fibres with porosity 80% and average pore diameter $2.2 \mu\text{m}$.

Thermally insulating hollow side-by-side bicomponent polyester fibres have been produced.²⁵ PET with $[\eta]$ 0.64 and PET with $[\eta]$ 0.58 were together melt-spun through a ring-shaped spinneret at 1:1 throughput ratio, drawn, crimped, heat-treated at 120 °C in the relaxed state, and cut to give hollow fibres with the degree of hollowness 5–30% and latent crimp 18/25 mm on heat-treating the fibres at 180 °C.

The author²⁶ has also documented the developments in acrylic fibres, wherein hollow acrylic fibres find their use in making insulative garments and in preparation of hollow fibre membranes for water treatment in food, pharmaceutical and electronic industries and in nuclear power plants. These fibres are also useful as precursors to carbon fibres, because they may dissipate heat more effectively than the conventional acrylic precursors.

Hollow acrylic fibres can be produced by a wet or dry spinning method or as bicomponents having sheath/core structure wherein the core is disposed or dissolved to get the hollow structure in the form of an internal linear continuous channel. Toray Industries has disclosed a process to manufacture hollow acrylic fibres by spinning a liquid containing acrylonitrile–methacrylic acid copolymer as a sheath and polyvinyl alcohol as a core. The resultant hollow acrylic fibre was used to produce hollow carbon fibres for use in composites.

4.2.3 Insulating structures with phase change materials

Phase change materials (PCM) absorb energy during the heating process as phase change takes place, otherwise this energy can be transferred to the environment in the phase change range during a reverse cooling process. The insulation effect reached by the PCM is dependent on temperature and time. PCMs as such are not new; they exist in various forms in nature. The most common example of a PCM is that of water at 0 °C, which crystallizes as it changes from a liquid to a solid (ice). A phase change also occurs when water is heated to a temperature of 100 °C, at which point it becomes steam. More than 500 different phase change materials have been documented by NASA.²⁷

However, use of the special thermophysical properties of PCMs to improve the thermal insulation of textile materials only became possible by entrapping them in microcapsules, each with a diameter of 1 μm to 6 μm .

Pause²⁸ has developed heat and cold insulating membranes for using on a roof structure. For this purpose, PCMs with a crystallization temperature between – 25 °C and 20 °C (Table 4.2) were selected to minimize the heat emission into the outside environment. Further, to reduce heat absorption from the outside environment, PCMs with melting points of 25 °C to 40 °C were chosen.

Table 4.2 Characteristics of phase change materials (PCM).
Temperature range from -25°C to 20°C

PCM	Crystallization point ($^{\circ}\text{C}$)
Dodecane	- 15.5
Tridecane	- 8.8
Tetradecane	- 0.2
Pentadecane	4.8
Hexadecane	- 12.2
Heptadecane	- 16.5
PCMs for temperature range 25°C to 40°C	
	Melting point ($^{\circ}\text{C}$)
Octadecane	28.2
Nonadecane	32.1
Eicosane	36.8
Heneicosane	40.5

Source: Ref. 28.

Vigo and Frost²⁹ pioneered the use of phase change materials for developing temperature-adaptable fabrics. Polyester, cotton, nylon 66 and wool fabrics were treated with an aqueous solution of polyethylene glycol (mol. wt. 600 or 3350) or one of the crystal materials (2,2-dimethyl-1,3-propanediol or 2-hydroxymethyl-2-methyl-1,3-propanediol). Such fabrics exhibited up to 250% greater thermal storage and release properties than the untreated ones. The energy storage capacity of hollow polypropylene fibres and viscose rayon filled with carbowax during thermal cycling between 230 and 330 K has also been demonstrated.

Vigo and Bruno³⁰ developed *NeutraTherm* fabrics, the first ever 'phase change clothing', by coating the fabric with PEG 1000, a polyethylene glycol waxy solid. The phase change of the fabrics lasts only about 20 min; after that, the garments revert to their original insulating properties. The PEG 1000 structure changes from soft to solid in keeping with the temperature, absorbing heat when it softens, and releasing heat when it solidifies. It is now reported that the lack of durability of such topical treatments to laundering and leaching, which remove the water-soluble polyethylene glycols, can be overcome by insolubilizing low-molecular-weight polyethylene glycols (average molecular weights 600–1000) on fabrics by their reaction with dimethylol dihydroxyethylene urea under conventional pad-dry-cure conditions to produce textiles that are thermally adaptable even after laundering.

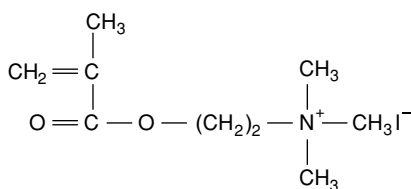
Acrylic fibres with increased latent heat retention have been prepared³¹ by treating wet-spun acrylic fibres in the swollen gelled state with substances having latent heat and having properties for transition from the solid state to

the liquid state, drying the fibres and heat-treating the fibre. Acrylonitrile-Me acrylate-sodium-2-(acrylamido)-2-methylpropanesulfonate copolymer was wet-spun, treated with an aqueous solution containing 50 g/l polyethylene glycol (I) to get a weight add-on of 6.2% dried, and heat-treated at 125 °C to give fibres with heat retention 33% as per the JIS L-1096 test.

Gateway Technologies³² has reported the application of heneicosane, eicosane, nonadecane, octadecane, and heptadecane as phase change materials for insulative fabrics. This material can be 425% as warm as a high bulk wadding. Schoeller Textil AG³³ Switzerland has also explored the application of micro-encapsulated phase change materials like waxes, which offer 'interactive' insulation for skiwear, snowboarding and ski boots. They store surplus heat and the wax liquefies; when temperatures drop, the microcapsules release the stored heat.

There are some hydrogels than can modulate the swelling ratio in response to environmental stimuli such as temperature, pH, chemical, photo-irradiation, electric field, etc. The collapse of a gel in response to environmental changes predicted by Dusek and Patterson,³⁴ was also investigated extensively by Tanaka et al.³⁵ Thermosensitive hydrogel collapses at elevated temperature through the lower critical solution temperature (LCST). The volume change occurs within a quite narrow temperature range. The permeability of water through the gel can be changed by an 'on-off' switch according to the environmental temperature. Therefore, such materials can be used as coatings for temperature adaptable fabrics, drug delivery systems and enzyme activity control.

Lee and Hsu³⁶ reported the swelling behaviour of thermosensitive hydrogel based on *N*-isopropyl acrylamide-trimethyl methacryloyloxy ethyl ammonium iodide (TMMAI) copolymers, a nearly continuous volume transition and associated phase transition from low temperature, and a highly swollen gel network to high temperature, a collapsed phase near its critical point between 31 and 35 °C. The gel with little TMMAI content (Table 4.3) showed a good reversibility and, the higher the TMMAI content (2–6%) in the copolymer, the higher the gel transition temperature.



TMMAI

Zhang and Peppas³⁷ have also studied the interpenetrating polymeric network (IPN) composed of the temperature-sensitive poly(*N*-isopropyl

Table 4.3 Characterization of NIPAAm/TMMAI copolymer gels

Sample	Feed composition (%)		Cloud point effect ^a	Cloud point temp. (°C)	Swelling ratio (g H ₂ O/g dry gel)
	NIPAAm	TMMAI			
TMM0	100	0	st	30–35	14.1
TMM1	99	1	st	30–35	19.3
TMM2	98	2	st	40–50	24.1
TMM3	97	3	vw	40–50	31.9
TMM5	95	5	vw	50–60	44.5
TMM6	94	6	vw	50–60	53.2

^ast, strong; vw, very weak.

Source: Ref. 36.

acrylamide)(PNIPAAm) and the pH-sensitive polymethacrylic acid (PMAA). The results showed that these hydrogels exhibited a combined pH and temperature sensitivity at a temperature range of 31–32 °C, a pH value of around 5.5, the pK_a of PMAA. The LCSTs of the polymers were significantly influenced by the polymer concentration. The addition of saccharides into aqueous polymer solutions decreased the LCST of all polymers. As the polymer concentration increased, the saccharide effects became more pronounced. A monosaccharide, glucose, was more effective than a disaccharide, maltose, in lowering the LCST, especially in Pluronic solutions.³⁸

The phase transitions of *N*-isopropylacrylamide and the light-sensitive chromophore-like trisodium salt of copper chlorophyllin copolymers induced by visible light has also been reported by Suzuki and Tanaka.³⁹ The transition mechanism in such gels is due only to the direct heating of the network polymers by light. As this process is extremely fast, such systems might be used as photo-responsive artificial muscles, switches and memory devices. All these phase change materials have great potential as coating materials in making skiwear, clothing for cold regions and high altitudes, etc.

4.3 Thermal insulation through polymeric coatings

Heat transfer can take place by means of conduction, convection or radiation across a barrier from the hot side to the cooler side. In conduction, heat passes from a hotter to a colder region along the static material. Convection is the transfer of heat by a flow of gases or liquids of different temperatures. In radiation, thermal energy is transmitted as electromagnetic waves.

PVC and PU are some of the widely used thermal insulators. They are invariably used in their foamed, expanded forms. The reason for this is the contribution of entrapped air or other gases to the total thermal insulation.⁴⁰

Table 4.4 Thermal conductivity of different substances

Materials	Thermal conductivity (mWm ⁻¹ K ⁻¹ at 20 °C)
Aluminium	200 000
Glass	1000
PVC tiles	700
Water	600
Brick	200
Fibres	200
Carpet	50
Clothing fabrics	40
Air (still)	25

Source: Ref. 40.

The total heat conduction λ_F of a polymeric material is the sum of components λ_G , λ_R , λ_S and λ_C , where G = gas in the cell, R = radiation across the cell of the foam, S = conduction through the wall and C = convection of the gas.

The highest resistance to heat flow comes from the air entrapped in the cell. Still air has one of the lowest thermal insulations, 25 mW/m K (Table 4.4). Therefore, polymeric materials in the form of foam have more entrapped air and show improved thermal insulation, the λ_S factor, which depends on the type of polymer itself and contributes approximately 30% of the total resistance to heat flow. Therefore, the type of polymer used in thermal insulators is the next major factor to be considered while designing a thermal insulator. The other two contributions, i.e. λ_R due to the radiation across the cell of the foam and λ_C due to the convection of the gas, is kept to optimum levels by proper design of the cell structure of the foam coating.

Requirements for extreme cold weather are:

- breathable membranes and coatings
- down and feather mixtures
- high-loft batting of special fibres
- reflective materials
- combinations.

4.3.1 Why breathable fabrics?^{41–44}

To avoid the condensation of perspiration in a garment, breathable fabrics are required. The garment can also become damp in rain or snowfall or in sportswear. The moisture diffuses through the clothing and can reach the human skin. As the moisture evaporates, the wearer feels cold and uncomfortable.

Table 4.5 Water vapour permeability data of polymeric coatings/films

Film	Cup method 20 °C, 95% RH (g/m ² 24 h)
Normal compact PUR	286
Microporous fluorocarbon	2140
Hydrophilic polyester	1290
Coated microporous PUR	1500–2000
Coated hydrophilic PUR	1000–1700
Grabotter film directly coated to the textile	1700–2000

Source: Gottwald L, 'Water vapor permeable PUR membranes for weatherproof laminates', *J. Coated Fabrics*, Jan 1996 **25**, 168–175.

A breathable fabric is waterproof and breathable because of the enormous difference between the size of a water droplet and a water vapour molecule. The former is 100 μm , in diameter whereas the latter is 0.0004 μm , i.e. there is a factor of around 250 000 between the two sizes.⁴¹

Waterproof/moisture permeable fabrics from several synthetic fibres have been designed for skiwear, track suits, rainwear, and mountaineering clothing. The application of a one-piece overall made from a woven nylon fabric (30-den flat nylon warp yarns; weft of 900-den air jet textured yarns) in the 1986 dogsled race in Alaska has been described. A nylon glove with a Gore-Tex liner was also designed for this purpose (Table 4.5).

Breathable fabrics can be classified into three main categories:

- coated fabrics
- laminated
- high-density woven fabrics.

4.3.2 Waterproof breathable coatings

The microporous barrier layer 'breathes' primarily through a permanent air permeable pore structure. Diverse techniques have been used to manufacture microporous coatings and films. The most important methods are listed below.

4.3.2.1 Mechanical fibrillation

For certain polymers, biaxial stretching produces microscopic tears throughout the membrane, which imparts a suitable microporous structure. For example, PTFE membranes are used in the Gore-Tex (two-layer and three-layer laminates). The thin microporous membrane is made from a solid PTFE sheet by a novel drawing and annealing process. In drawn form, the tensile strength is increased threefold. The manufacturers claim that these PTFE membranes

contain approximately nine billion pores per square inch, with a pore volume of up to 80% and a maximum pore size of 0.2 μm .

4.3.2.2 *Solvent exchange*

In this process, a polymer dissolved in a water miscible solvent is coated thinly onto the fabric. The porous structure is developed by passing through a coagulation bath where water displaces the solvent. For example, the textile substrate is coated with polyurethane solution, where DMF is used exclusively as the solvent, and the fabric is passed through a coagulation bath containing water, where water displaces the solvent to give a porous structure.

4.3.2.3 *Phase separation*

The coating polymer is applied from a mixture of a relatively volatile solvent with a proportion of higher boiling non-solvent. Precipitation of the polymer as a microporous layer occurs as the true solvent evaporates faster during the subsequent drying process. For example, the polyurethane-based Ucecoat 2000 system operates on this principle. Here, a lower boiling solvent (methyl ethyl ketone) evaporates preferentially as the fabric passes through the oven, thereby increasing the concentration of the non-solvent in the coating. When the concentration of the non-solvent reaches a critical level, the polyurethane precipitates out in a highly porous form and the remainder of the solvent and the non-solvent evaporate from the coating as the fabric passes through the oven.

The fabrics useful for apparel for keeping the body warm in cold weather or for sporting have porous polyurethane-based films. Nylon fabric penetrated with Asahiguard 710 was coated with polyurethane, hardener, DMF and hydrophobic silica (0.016 μm size) and washed with water. It was then printed with polyurethane and sodium stearate-treated α -alumina, dried at 100 °C for 2 min, and later impregnated with F-type water repellent, dried and set at 170 °C for 30 s. This treated fabric showed moisture permeability 7630 g m^{-2} 24h and thermal conductivity 4.1 $\text{W cm}^{-1} \text{ }^\circ\text{C}^{-1} \times 10^{-4}$.

4.3.2.4 *Solvent extraction*

Finely divided water soluble salts or other compounds can be formulated into the polymer and subsequently extracted from the dried film or coating with water to get a microporous structure.

4.3.2.5 *Electron bombardment*

A process has been developed for rendering the solid coated fabrics microporous by bombarding the polymer coating with electron beams. The technique

Table 4.6 Water vapour resistance of clothing fabrics for comparison

Fabrics	Water vapour resistance (mm still air)
PVC coated	1000–2000
Waxed cotton	1000+
Leather	7–8
Typical non-wovens	1–3
Woven microfibre (nylon or polyester)	3–5
Closely woven cotton	2–4
Ventile L28	3–5
Two-layer PTFE laminates	2–3
Three-layer laminates (PTFE, PE)	3–6
Microporous PU (various types)	3–14
Open pores	3–5
Sealed pore	6–14
Hydrophilic PU coated	4–16
Witcoflex staycool in nylon, polyester	9–16
On cotton, poly/cotton	5–10

Source: Handbook of technical textiles, Ed Horrocks A R and Anand S C, Woodhead Publishing, UK, 2000, 304.

involves feeding the coated fabric between two electrodes, generating high voltage electrons which can be focused into discreet beams which drill through the coating without damaging the fabric beneath.

4.3.2.6 UV-EB curing

The sunbeam process is used to manufacture microporous films and coatings in-situ by cross-linking suitable monomers with electron beam or UV light. Radiation curing has the following advantages over the conventional methods:

- low energy consumption
- low environmental pollution
- fast curing and thus fast processing
- short start-up times.

4.3.2.7 Crushed foam coating

Mechanically foamed and thickened lattices are coated onto fabric and dried. Large surface pores are formed, which are compacted by calendaring through a pressure nip which yields a microporous fabric. The water-vapour permeability values of various polymeric coatings are given in Table 4.6.

Woods has studied the relation between clothing thickness and cooling

Table 4.7 Some commercially available insulation materials

Products	Manufacturer	Characteristics	End use
Drylete®	Hind	Combines Hydrofil nylon and hydrophobic polyester to push moisture away from the body and then pull it through fabric for quick drying	Skiwear, running and cycling apparel
Gore-Tex®	W. L. Gore	The original waterproof/breathable laminated fabric with pores large enough for water to escape, small enough to block rain	Outerwear, hat, gloves, footwear, running and cycling apparel
Hydrofil®	Allied	A new super-absorbent hydrophilic nylon that sucks moisture away from the skin	Linings, long underwear, cycling apparel
Silmond®	Teijin	A durable water repellent and windproof fabric made from polyester microfibrils	Outerwear
Synera®	Amoco	A strong, lightweight polypropylene fabric that transports moisture away from the skin	Long underwear, jacket lining
Supplex® Tactel	DuPont	Extremely soft, quick drying nylon in smooth or textured version apparel	Outerwear, skiwear, running and cycling apparel
Thermolite®	DuPont	An insulation made of polyester fibres that have been coated	Skiwear, climbing apparel
Thermoloft®	DuPont	A semithick insulation that contains hollow polyester fibres that trap warm air	Skiwear, outdoor apparel
Thinsulate®	3M	Thin insulation made of polyester and polypropylene fibres	Skiwear, gloves, footwear
Thintech®	3M	A waterproof/breathable laminated fabric that is highly resistant to contamination by detergents or perspiration	Skiwear, outerwear

Source: Ref. 40.

during motor-cycling in the range from -1 to 24°C . To maintain a normal body temperature in winter on a motor-cycle without a protective shield, much thicker clothing (mean clothing thickness of 20 mm) inside windproof oversuit is needed at 5°C , but it is only effective if perspiration does not accumulate inside the clothing.

4.3.3 Waterproof breathable membranes

4.3.3.1 *Composition*

Microporous film fully impregnated with a hydrophilic polymer, Thintech, is sandwiched between the outer and inner fabrics of a garment, followed by lamination of Thintech to their Thinsulate Thermal Insulation.

4.3.3.2 *Application*

It prevents rain, sleet or snow from penetrating a garment and stops the build-up of moisture within the garment.

4.3.4 Antistatic and heat energy-absorbing coatings

The coating comprises 5–90% ultrafine Sb–Sn oxide particles (from $< 0.1\ \mu\text{m}$ Sb_2O_3) and 10–90% binder resin.

Polyester cloth treated with aqueous acrylic emulsion (acrylic melamine resin) containing 20% of $0.005\ \mu\text{m}$ ATO particles and baked to form a cloth showing the half-life of an electric charge of one sec. The front and back temperatures are 27°C and 26°C , respectively, after irradiating with 300 W lamp at 20°C and 60% RH.⁴⁵

Heat-insulating, moisture-permeable, and water-resistant nylon⁴⁶ has been produced by coating it with polyurethane containing 2–4% of inorganic fine powder (Sb oxide-doped SnO_2) and Zr carbide having photoabsorption thermal conversion capability. The coated nylon fabric showed water resistance pressure (x) $\geq 7000\ \text{g/m}^2$ 24 h and moisture permeability (y) $\geq 0.6\ \text{kg/cm}^2$.

Bonding of IR-ray radiating ceramics has also been attempted for producing thermal insulative textiles. Insulating fabrics were prepared by immersing fabrics in emulsions containing IR ray-radiating ceramics and polymers and adding trivalent metal salts to the emulsion to cause bonding of the ceramic to the fabrics.⁴⁷ Thus, a fabric was immersed in a dispersion containing synthetic rubber latex (solids 15%) and 10% (on fabric) IR ray-radiating ceramic, and stirred as 10% $\text{Al}_2(\text{SO}_4)_3$ was added dropwise,

washed and dried to give an odour-absorbing insulating fabric with ceramic content of 10%.

The thermal insulation capabilities of cold protective clothing materials may be significantly improved by the application of MicroPCM, that is capsules containing small amounts of PCM (phase change materials). The PCM have the ability to changing their state within a certain temperature range, storing energy during the phase change and then releasing it at crystallization temperature. It is shown that, by applying a coating of 50 g/m^2 onto a fibrous batting of 180 g/m^2 , the insulation capacity is comparable to a batting of 360 g/m^2 . Micro PCM may thus be used to increase the insulation capabilities against the cold, with a resulting material which will be significantly thinner, allowing much larger freedom of movement.²⁸

4.4 Designing of fabric assemblies^{48–55}

In colder environments, layered fabrics rather than a single fabric are used in most cases (Table 4.7). Under such conditions, the two most important characteristics of fabrics are water vapour and heat transport. In order to gain insight into the transient states of such transport across a set of layers of fabrics, Yasuda et al.⁴⁹ developed an MU water vapour transport simulator (MU–WVT simulator). They reported that water transport was not influenced significantly by surface characteristics – the hydrophilic or hydrophobic nature of fabrics. On the other hand, when liquid water contacted a fabric, such as in the case of sweating, the surface wettability of the fabric played a dominant role in determining the water vapour transport rate through the layered fabrics. In such a case, the wicking characteristic, which determines how quickly and how widely liquid water spreads out laterally on the surface of/or within the matrix of the fabric, determines the overall water vapour transport rate through the layered fabrics.

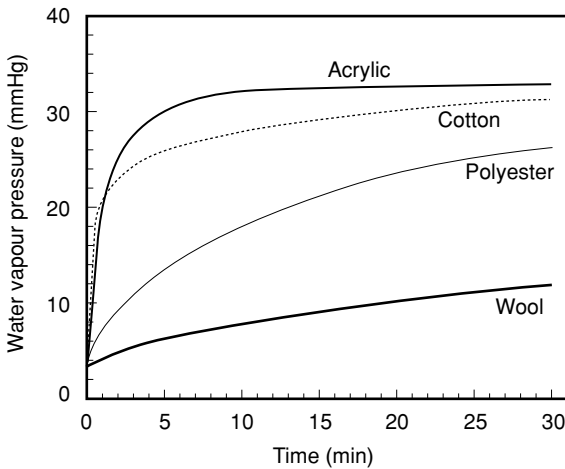
The overall water vapour and heat transport characteristics of a fabric should depend on other factors such as the water vapour absorbability of the fibres, the porosity, density and thickness of the fabric, etc. In this study, the major emphasis was on the influence of the chemical nature of the fibres that constitute a woven fabric. Dynamic water vapour and heat transport in the transient state were investigated for fabrics made of polyester, acrylic, cotton and wool fibres (Table 4.8). The overall dissipation rate of water vapour depends on both the vapour transport rate and the vapour absorption by fibres, which are mutually interrelated. Water vapour transport is governed by the vapour pressure gradient that develops across a fabric layer (Fig. 4.2). When a fabric is subjected to given environmental conditions, the actual water vapour transport rate differs greatly depending on the nature of the fibres, even

Table 4.8 Characteristics of fabrics

Property	Polyester	Acrylic	Cotton	Wool
Fabric density ^a (cm ⁻¹)				
Ends	36.4	37.0	38.1	34.9
Picks	22.5	22.1	23.8	24.4
Thickness ^a (mm × 10)	2.7	2.9	3.1	3.2
Weight ^a (g/m ²)	121.7	116.4	125.0	113.9
Porosity ^a (%)	67.5	66.4	74.8	73.4
Air permeability ^a (cm ³ /cm ² /s)	77.8	81.0	28.2	54.9
Advancing contact angle of water	116	^b	^c	116
Water vapour absorption rate (g/g/min × 10 ⁴)	3.3	6.1	10.1	15.0

^aAccording to JIS (Japanese Industrial Standard) L 1096. ^bWater droplet was absorbed by the fabric gradually. ^cWater droplet was absorbed by the fabric immediately.

Source: Ref. 49.



4.2 Comparison of water vapour build-up curves in chamber 1 in the sweat (liquid water) case. Source: ref. 49.

when other parameters are nearly identical, such as density, porosity and thickness.

Hong et al.⁵⁰ have studied in-depth dynamic moisture vapour transfer through clothing assemblies. Cotton, polyester and a blend in plain woven, pure finish fabrics were studied to determine their influence on dynamic surface wetness and moisture transfer through textiles. A simulated sweating skin was used, over which were placed test fabrics incorporating a clothing hygrometer to continuously measure dynamic surface wetness. Moisture

vapour concentration and its rate of change at both inner and outer fabric surfaces were determined. At the inner fabric surface facing the sweating skin, all the cotton fabric exhibited the slowest build-up of moisture vapour concentration, followed by cotton/polyester blend. The all-polyester fabric showed the highest rate of change in moisture vapour concentration. The newly modified clothing hygrometer provides a sensitive method for ascertaining dynamic surface wetness on both fabrics and clothing as worn.

Dynamic moisture vapour transfer through textiles has also been investigated by Kim.⁵¹ The influence of semipermeable functional films on the surface vapour pressure and temperature of fabric–film–fabric assemblies has been reported. The film added between two fabric layers affects vapour pressure and temperature changes on both surfaces of the assembly under simulated body-clothing conditions. The physical characteristics of films greatly influence the level of transient, comfort-related variables such as changes of inner surface vapour pressure and temperature. Mixed cotton and polyester layers of a film reveal that the film can negatively affect the moisture sorption of the assembly, not only by blocking the air spaces for moisture diffusion but, more importantly, by ineffective heat dissipation from the cotton inner fabric for continued moisture sorption. Using film and fabric assemblies, this study reinforces the interdependence of moisture sorption and temperature barrier effects during dynamic moisture transfer through the clothing assemblies. The percentage increases of moisture uptake of C/P (inner/outer) and P/C (inner/outer) without any film (none) are the same throughout the experiment (0.7, 1.6, 2.2 and 2.7%). The presence of films, however, produces different moisture uptake behaviours in the C/P and P/C (Fig. 4.3).

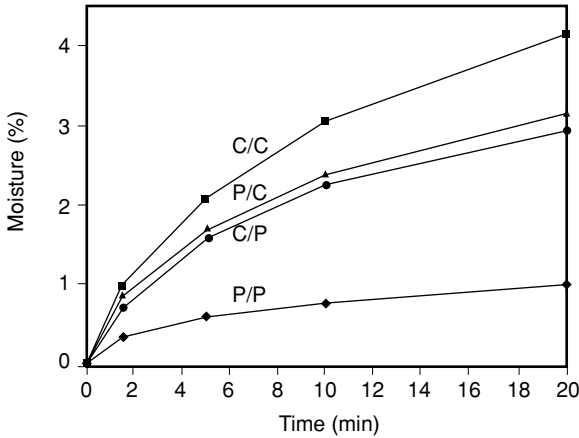
The thermo-insulating properties of lofty non-woven fabrics, which have been reported in several papers, depend on the nature of pore size and distribution in a fabric, which are a function of fibre fineness and material density. Jirsak et al.⁵² compared in a more comprehensive way the thermo-insulating properties of both perpendicular-laid and conventional cross-laid nonwoven fabrics. The total thermal resistance R of a textile fabric as a function of the actual thickness of the material:

$$\lambda_{\text{total}} = \lambda_{\text{sa}} + \lambda_{\text{r}} \quad [4.2]$$

$$R[\text{m}^2\text{KW}^{-1}] = L/\lambda_{\text{total}} \quad [4.3]$$

where λ_{total} is the thermal conductivity ($\text{Wm}^{-1}\text{K}^{-1}$) as defined in Eq. (4.2), λ_{sa} is the combined thermal conductivity of solid fibre and air and L is the thickness of the sample (m). The thickness of the material depends on the compression P (Pa):

$$L = L(P) \quad [4.4]$$



4.3 Dynamic moisture uptake, as a function of time, measured on fabric–film–fabric assemblies. *Source:* ref. 51. C/C = cotton/cotton double-knit assembly, P/P = polyester/polyester assembly.

Thus, materials showing the same λ_{total} value, those with higher compressional resistance, will exhibit better thermal resistance under the same compression. The perpendicular-laid fabrics, due to their unique fibre orientation, demonstrate a higher degree of compressional resistance in the thickness direction than the cross-laid ones.

Farnworth⁵³ also presented a theoretical model of the combined conductive and radiative heat flows through fibrous insulating materials and compared them with experimental values of the thermal resistances of several synthetic fibre battings and of a down and feather mixture (Table 4.9). No evidence of convective heat transfer is found, even in very low-density battings. The differences in resistance per unit thickness among the various materials may be attributed to their different absorption constants.

Crews et al.⁵⁴ evaluated the use of milkweed floss as an insulative fill material and compared its performance to other insulators. Seven identical jackets were constructed using different fill materials matched on a per unit weight basis. The insulation (clo) values for the jackets were measured using a standing, heated manikin as an environmental chamber. Thickness (loft), compression, resiliency and hand were also measured. The results show (Table 4.10) that milkweed floss blended with down has insulative properties similar to down. Down is superior to milkweed floss in loftiness and compressibility, which influence product performance, but the properties of milkweed floss can be enhanced by blending it with down.

Table 4.9 Physical and thermal properties of all samples studied at minimal compression (0.16kPa)

Sample	Fibre material	Fibre radius (μm)	Thickness (mm)	Mass (kg/m^2)	Fibre volume (%)	Thermal resistance $\text{m}^2\text{K}/\text{W}$
Polarguard	Polyester	11.7	26	0.270	0.76	0.48
Hollofil	Polyester	13.2	28	0.350	0.94	0.59
Thinsulate M400	Polypropylene	1 to 3	7.7	0.405	5.8	0.25
Thinsulate C150	Polypropylene and polyester	1 to 3 20	5.2	0.175	~3.0	0.16
Down and feathers	40% and 60%	—	42	0.545	~1.3	1.22

Source: Ref. 53.

Table 4.10 Insulative value for filling material type before and after cleaning

Fill type	Insulation value I_T (clo)	
	Before cleaning	After cleaning
50% Milkweed floss/50% down	2.36	2.26
100% Down	2.28	2.25
100% Quallofil	2.26	2.19
100% Milkweed	2.24	2.16
50% Milkweed/50% feathers	2.24	2.06
100% Thinsulate	2.15	2.04
60% Milkweed/40% olefin	2.04	1.97

Source: Ref. 54.

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Cross-linked polyol fibrous substrates as multifunctional and multi-use intelligent materials

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DEVRON P. THIBODEAUX

5.1 Introduction

The concept of ‘intelligent’ or ‘smart’ materials was critically reviewed within the context of fibrous materials having these attributes. It is generally agreed that the development of such materials occurred first with shape memory metal alloys (in the 1960s), followed by studies on polymeric intelligent gels (1970s). Also, a few studies were initiated in the late 1970s and early 1980s on intelligent fibrous materials.¹ This study will briefly review fibrous materials that possess this special attribute, which is usually defined as a profound change caused by an external stimulus that may or may not be reversible. Also examined in detail are our recent investigations on fibrous materials containing bound polyols that have at least two intelligent attributes: thermal and dimensional memories. Particular attention is focused on the techniques for measurement and characterization of load and pressure development in modified fabrics wet with polar solvents, and possible applications for these materials.

5.2 Fibrous intelligent materials

Although intelligent fibrous substrates were first described and demonstrated in Japan in 1979 with shape memory silk yarn,² it is our opinion that the discovery of crease recovery in cellulosic fabrics in the wet and dry state by Marsh and coworkers in 1929 was actually the first example of intelligent materials that even preceded intelligent shape memory alloys.³ However, this discovery, which later led to the commercialization of durable press fabrics, was never identified or promoted as an intelligent textile concept.

The shape memory silk yarn was modified by immersion in a hydrolysed protein solution, followed by subsequent drying, crimping, immersion in water and heat setting at high pressure in the wet state. On subsequent heating at 60 °C, the yarn becomes bulky and crimped, but it reverts to the untwisted and

uncured state upon drying.² Two other important developments that were patented in the late 1980s can be classified as intelligent fibrous materials. The first was polyester or polyamide fabrics, which absorbed visible solar radiation and converted it into heat as infra-red radiation released inside the garment due to the microencapsulation of zirconium carbide; it was irreversible since it did not reverse at high temperatures to provide cooling.² The second was thermochromic garments (colour change induced by incorporation of compounds that respond to changes in environmental temperature) produced by Toray Industries⁴ called SWAY, which have reversible colour changes at temperature differences greater than 5 °C and are operable from - 40 °C to + 80 °C.

Most of the other recent investigations on intelligent fibrous materials have been primarily concerned with shape memory effects. Some relevant examples are polyester fabrics with durable press properties produced by high energy radiation cross-linking with polycaprolactone and acrylate monomers⁵ and temperature-sensitive polyurethanes prepared by copolymerization of polytetramethylene glycol and methylene diisocyanate, 1,4-butanediol.⁶ More novel intelligent fibre applications and responses to external stimuli were described in a 1995 American Chemical Society symposium. These polymeric smart materials included fibre optic sensors with intelligent dyes and enzymes whose fluorescence changes with changes in glucose, sodium ion and pH, and elastomeric composites embedded with magnetic particles, which undergo changes in their moduli when exposed to external magnetic fields and thus can be used for vibration or noise reduction in transportation and machinery.⁷ Smart fibrous composite sensors made of carbon and glass have also been described for prevention of fatal fracture by changes in their insulating and conductive properties.⁸

Fibrous materials containing bound or cross-linked polyols were patented and initially characterized by multifunctional properties imparted to the modified materials by a single process.^{9,10} Major property improvements include thermal adaptability, high absorbency and exsorbency, enhanced resistance to static charge, oily soils and flex abrasion, and antimicrobial activity. The most notable of these property improvements was temperature adaptability and reversibility due to the phase change material (PCM) characteristics of the cross-linked polyol bound to the fibres. However, this unique and new fibre property was not initially defined as an intelligent material attribute. Moreover, a related invention, the disclosure of fibres with thermal adaptability due to attachment by microencapsulation of hexadecane and *n*-eicosane (PCMs with high latent heat and thermal reversibility), was also not characterized as an intelligent fibrous material.¹¹

5.3 Experimental

The modified fabrics containing the bound polyols, derived from using formulations with different molecular weight, acid catalysts and cross-linking resins as previously described,¹³ were woven cotton and 65/35 cotton polyester printcloth or sheeting (125–135 g/m²). The surface temperatures were measured with a Hughes Probeye Thermal Video System 3000 with an image processor, infra-red camera head, argon gas cylinder and colour screen monitor. Untreated and modified fabrics (6 in² or 150 mm²) were mounted on a pin frame surrounded by a wooden enclosure containing a 150 watt light bulb whose heat output was controlled by a voltage regulator device (Variac) with the camera sensitivity set at 2.0 and emissivity value set at 0.95, which was appropriate for fabric surfaces. Surface temperatures (°F) were measured every 10 min and for up to 30 min with the infra-red camera 1 m from the fabric by positioning the cross-hairs of the camera in the centre of the fabric with the untreated control value at 147 °F (64 °C).

For the work and power measurements previously described,¹³ a 65/35 cotton/polyester cross-tuck knit (177 g/m²), woven cotton printcloth (125 g/m²), and 50/50 hydroentangled pulp/polyester non-woven (80 g/m²) containing 40–60% bound polyol were evaluated. Each of the fabrics was attached to a metal alligator clip, suspended vertically. The amount of shrinkage, work (W) performed, and power (P) generated were determined with weights attached after wetting with various solvents (water, acetone and ethanol). The amount of shrinkage was also determined without weights attached for each of the different types of fabrics for each solvent.

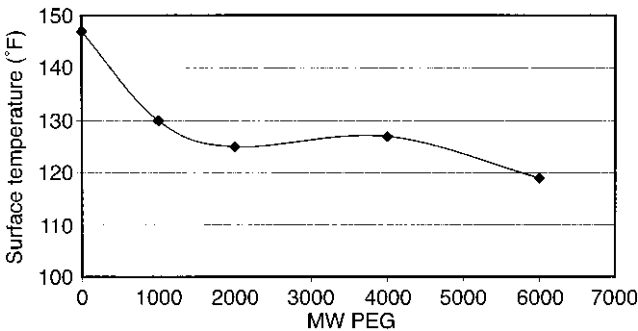
For the tension and pressure measurements, a desized, scoured and bleached 100% cotton interlock knit fabric (205 g/m²) was treated with 50% PEG-1450–11% DMDHEU (Fixapret ECO)–5.1% citric acid–5.1% MgCl₂·6H₂O to a wet pickup of 110%, then cured for 3 min at 110 °C, washed in warm water to a pH of 8.5 to neutralize acid catalyst, excess water removed, then oven-dried for 7 min at 85 °C. The resultant fabric had a wt. gain of 65% and had shrinkage in one direction (longitudinal) when wet with various polar solvents (28% with water; 25% with 1% aq. NaCl; 10% with 95% ethanol; and 7% with acetone). Three inches of a 1 × 6 inch strip of the treated fabric was clamped between the jaws of an Instron (Model 4201) having a 10 lb load cell, completely wet with each of the four solvents and tension load/stress measured after initial wetting to a maximum time of 15 min.

5.4 Results and discussion

5.4.1 Thermal memory

The characterization of fibrous materials containing cross-linked polyols as smart materials with a thermal memory was first discussed by Vigo in an American Chemical Symposium which he co-organized in 1995⁷ and later described in more detail in conference proceedings and in refereed journals.^{12,13} This thermal memory or thermal reversibility is unique and has been determined and documented by differential scanning calorimetry and infra-red thermography. The latter measures changes in surface temperature on exposure to a heat source. As shown in Fig. 5.1, cotton fabrics containing bound polyol had substantial reduction in surface temperature relative to an untreated control fabric (surface temperature 147 °F or 64 °C) after all fabrics were exposed to a heat source for a minimum of 30 minutes. Even more impressive is that the lowest amounts of bound polyol in the fabric gave the greatest decrease in surface temperature. Weight gains were 34% for fabrics containing bound PEG-1000, 37% for fabrics containing bound PEG-2000, 28% for fabrics containing bound PEG-4000 and only 25% for fabrics containing bound PEG-6000.

The decrease in surface temperature in all treated fabrics usually occurred within 30 seconds and was greater with higher molecular weight cross-linked polyols bound to the fabric, due to the increasing crystallinity of the polyol with increasing molecular weight. Surface temperature decrease on the modified fabrics was 17–28%. Thermal memory and reversibility have been documented in commercial skiwear marketed in Japan, with the crosslinked polyol as one of the fabric components; thermocouples in this component demonstrated that the skiers had optimum thermal comfort by an increase in fabric surface temperature when idle and lowering of the surface temperature after skiing, thereby preventing discomfort due to perspiration and body heat.¹⁴

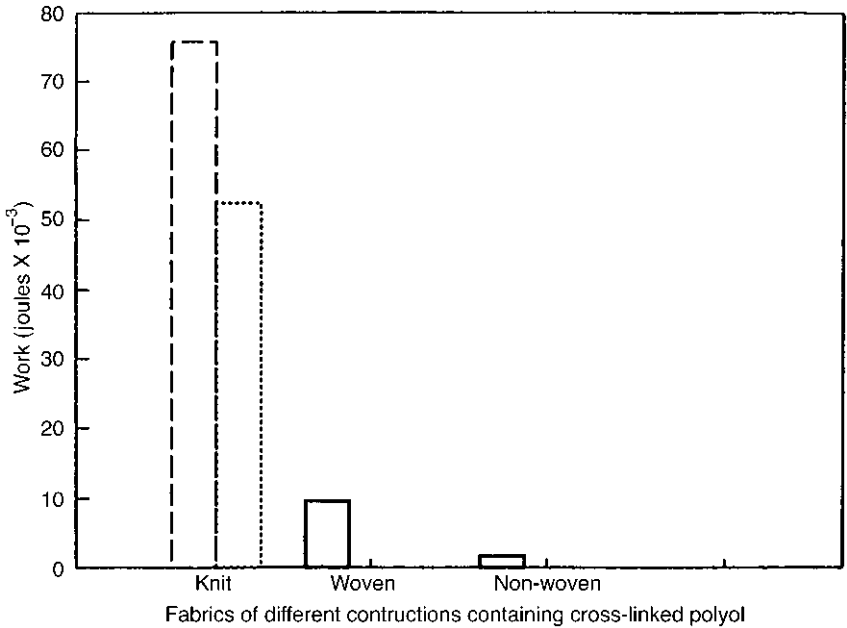


5.1 Change in surface temperature of untreated and cross-linked polyol-treated fabrics after 30 min exposure to a heat source.

Applications for thermally adaptable fabrics containing cross-linked polyols have been previously described, primarily with regard to apparel and insulation.¹⁰ However, there are many other applications that could evolve based on the ‘intelligent’ thermal memory of these modified fibrous materials. The wear life of many automotive and aerospace components could be extended by the moderation of temperature fluctuations during their use. Camouflage uniforms made of this material would be useful for the military because the wearer would have a different surface temperature on garments normally detected by infra-red sensors. The thermal buffering capacity of the modified fabrics could be used advantageously in various healthcare applications, such as in burn therapy and to improve skin temperature and circulation in patients with maladies such as arthritis and diabetes. Changes in the fabric surface temperature could also be used to fabricate remote sensing devices for detection in industrial, residential, horticultural, agricultural and other environments where temperature change detection would be useful. These modified fabrics could be used to minimize plant stress due to temperature changes and fluctuations as well as protection of livestock and other animals. Many other ‘thermal memory’ applications for these modified materials as sensors and/or actuators are envisioned with the molecular weight of the bound polyol defining the magnitude and temperature range desired.

5.4.2 Dimensional memory

It was known from our earlier studies that certain types of fabric constructions containing bound polyol were more prone to wet shrinkage. The magnitude of this effect with various solvents such as hexane, ethanol, acetone and water, was investigated with three different fabric constructions: knit, woven and non-woven.¹³ An increase in the polarity of the solvent resulted in increasing reversible wet shrinkage (highest with water, no shrinkage with hexane) that was most pronounced with knit fabric constructions. To demonstrate the potential for converting chemical into mechanical energy, different quantities of weights were affixed to modified knit, woven and non-woven fabrics that were subsequently wet with water. The work performed (W) and power generated (P) were determined. As shown in Fig. 5.2, knit fabrics are far superior to woven and non-woven fabrics in this characteristic, due to its optimum wet shrinkage in the presence of an applied force. Work performed by the wet knit fabric was 30–50 times greater than that of the non-woven and woven fabrics when each had the same amount of weight attached (50 g). It was even an order of magnitude greater when the knit fabric had twice the weight attached compared to the other two fabrics. Similar results were obtained for power generated (P). These results were used to present the concept and design of an intelligent medical bandage that would contain a removable and



5.2 Work (W) performed by fabrics of different constructions containing cross-linked polyol by lifting attached weights after wet with water for 30 s. — +50 g, - - - +100 g, ... +200 g (from ref. 13).

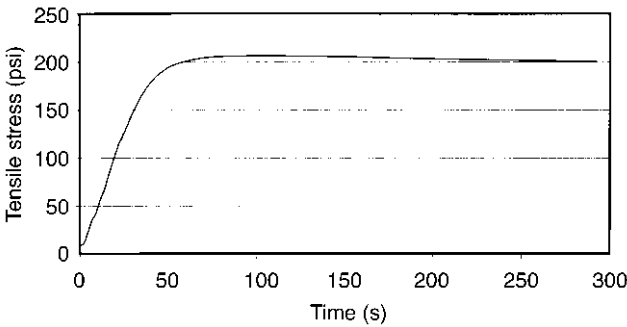
disposable component of knit cross-linked polyol fabric affixed to a non-disposable component by metal fasteners or other methods.¹⁵ However, no pressure or tension measurements were made to determine the amount of tension or force developed for these types of intelligent fabrics with dimensional memories activated by wetting with polar solvents.

The tensile load (lb) and stress developed (psi) were measured for untreated and treated fabric strips after wetting with deionized water (Table 5.1). The tension developed for the untreated fabric was negligible, but it was very significant for the treated fabric. Multiple measurements were made and there was some detectable variability (a range of 4.5–5.6 lb and corresponding values of 130–196 psi). In addition to the development of high tensile stress, the modified fabrics wet with water achieved these values rapidly (within 90 seconds of wetting) and maintained them over the measurement period of 5 min (Fig. 5.3). Although there was somewhat more variability for treated fabrics that were wet with 1% aq. NaCl with regard to load and tensile stress developed (3.5–6.2 lb and 120–217 psi), these fabrics also developed such tension rapidly (Fig. 5.4). Thus, tension developed rapidly in treated fabrics wet with water and aqueous salt solution and was generally proportional in

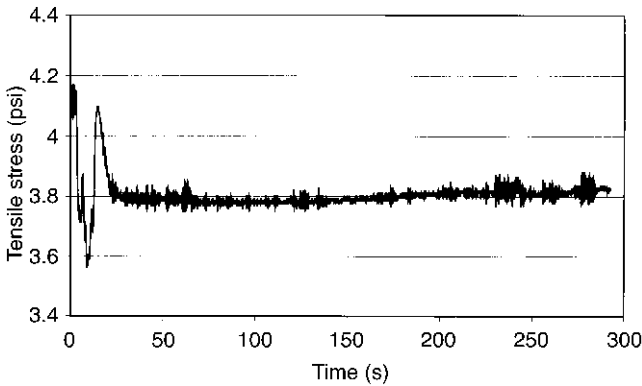
Table 5.1 Maximum load and tension developed in fabrics after wetting with aqueous solvents^a

Fabric	Solvent/solution	Max. load (lb)	Max. tension (psi)
Untreated control	H ₂ O	—	—
Treated	H ₂ O	5.6	196
Treated	1% aq. NaCl	6.2	217

^aAll fabrics were clamped between jaws of Instron (1 × 3 in length) that were wet within 30 s and tension developed measured from initial wetting up to 5 min.



5.3 Development of tension over time with modified fabric after wetting with water.



5.4 Development of tension over time in untreated control fabric after wetting with water.

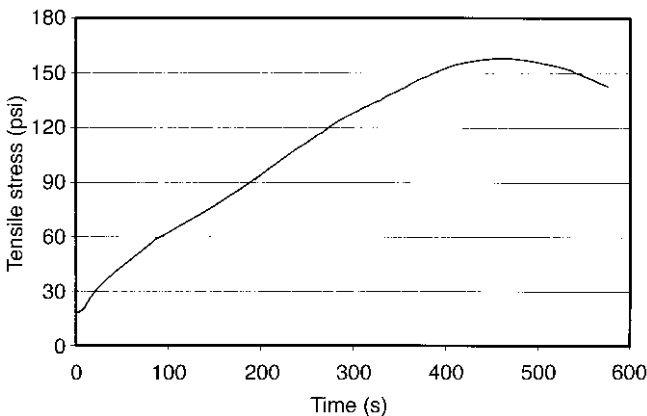
magnitude to the wet shrinkage that these fabrics experienced when they were not constrained.

The behaviour of the modified fabrics when wet with the two organic solvents shown in Table 5.2 and Fig. 5.5 and 5.6 (95% ethanol and acetone, respectively) differed from those wet with aqueous media in three fundamental aspects: (1) maximum tension took longer to achieve with these solvents than those wet with aqueous media; (2) the tension developed was also less than those exposed to aqueous media; and (3) the reversal of load and pressure occurred over relatively short time periods due to the high vapour pressure and accompanying evaporation of solvent. Fabrics wet with ethanol took about 450–550 seconds to reach maximum stress (138 psi generated), then reversed this effect due to slow solvent evaporation (Fig. 5.5). Fabrics wet with acetone reach maximum tension more rapidly (150 seconds with a corresponding load of 1.6 lb and 56 psi), but rapidly reversed back to zero load after 250 seconds due to the complete evaporation of the solvent (Fig. 5.6).

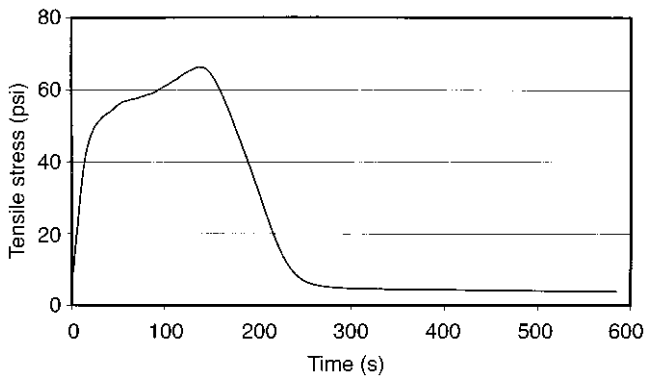
Table 5.2 Maximum load and tension developed in fabrics after wetting with polar organic solvents^a

Fabric	Solvent	Max. load (lb)	Max. tension (psi)
Treated	95% ethanol	3.9	138
Treated	Acetone	1.6	56

^aAll fabrics were clamped between jaws of Instron (1 × 3 in length) that were wet within 30 s and tension developed measured from initial wetting up to 15 min.



5.5 Development of tension over time in modified fabric after wetting with ethanol.



5.6 Development of tension over time in modified fabric after wetting with acetone.

Intelligent fabrics containing cross-linked polyols that have reversible dimensional memories on exposure to polar solvents can serve in a variety of applications. A variety of sensors could be developed that detect different types of polar solvents and solutions related to the amount of wet shrinkage and/or tension developed. Alternatively, fabric sensors could be fabricated to detect varying amounts of water vapour and liquid water by wet shrinkage and/or accompanying tension developed on wetting. Several types of actuator systems based on these modified fabrics are also envisioned. In the biomedical and healthcare area, wetting with solvents such as sterilized water, salt solutions and alcohol could be used to activate medical pressure bandages and possibly tourniquets; alternatively, blood (plasma) could activate pressure development and thus stop undesirable bleeding. These fabrics could be used to produce micromotors and a variety of valves or other mechanical devices that are activated by the reversible wet shrinkage that occurs with a variety of polar solvents.

5.5 Conclusions

Fabrics of woven, non-woven and knit constructions containing cross-linked polyols have been shown to have thermal memories over a wide temperature range and can be adapted to various thermal environments by the molecular weight of the bound polyol and the degree of cross-linking on the fibrous substrate. In contrast, only specific fabric constructions (cross-tuck and interlock knits) containing the cross-linked polyols are able to generate substantial tensile load when wet with polar solvents. The load and stress generated are usually proportional to the degree of wet shrinkage when the fabrics are not constrained. Maximum and rapid tension development occurs

with water and aqueous salt solutions, while ethanol and acetone are somewhat less effective with faster reversibility due to rapid evaporation of these low-boiling, high vapour pressure solvents. Numerous applications for the cross-linked polyol fabrics with thermal and dimensional memories are envisioned with two major areas of use as sensors and actuators.

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Stimuli-responsive interpenetrating polymer network hydrogels composed of poly(vinyl alcohol) and poly(acrylic acid)

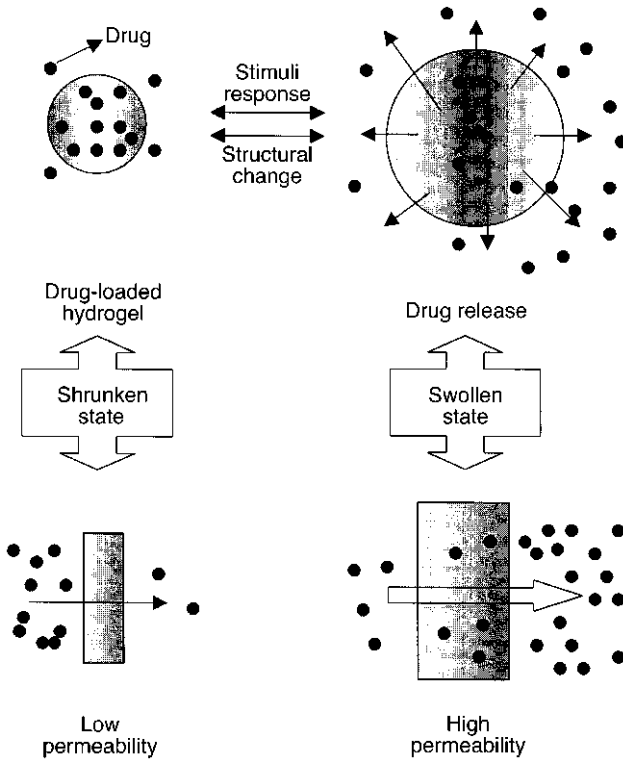
YOUNG MOO LEE AND SO YEON KIM

6.1 Introduction

Recently, there have been many investigations of stimuli-responsive hydrogels, which are three-dimensional polymer networks exhibiting sensitive swelling transitions dependent on various stimuli, e.g. electric field,^{1,2} pH,^{3–7} temperature,^{8,9} ionic strength¹⁰ or other chemicals.^{11,12} They have been considered to be useful in separation and medical applications, especially in drug delivery systems.

The schematic diagram illustrating the diffusion of bioactive materials through stimuli-sensitive hydrogels is shown in Fig. 6.1. Among these, pH and/or temperature-responsive systems have been potential candidates because these factors could be the most widely available in the environment of the human body. In an aqueous system, the temperature dependence of the swelling of a polymer gel is closely related to the temperature dependence of polymer–water and polymer–polymer interaction. Katono et al.¹³ investigated thermal collapse from interpenetrating polymer networks (IPNs) composed of poly(acrylamide-*co*-butyl-methacrylate) and PAAc, and obtained on–off release profiles as a function of temperature. Poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels demonstrated negative temperature sensitivity with lower critical solution temperature (LCST) in aqueous solution, which showed the decrease of swelling with an increase of the temperature above 30–32 °C.¹⁴

In the case of pH-dependent drug delivery systems, many researchers have focused on the swelling properties of hydrogels. The acidic or basic components in the hydrogels led to reversible swelling/deswelling because they changed from neutral state to ionized state and vice versa in response to the change of pH. Brannon and Peppas¹⁵ reported a pH-sensitive drug release system composed of a copolymer of hydroxyethyl methacrylate (HEMA) and methacrylic acid (MAAc) or maleic anhydride. The poly(NIPAAm-*co*-vinyl terminated poly(dimethylsiloxane)-*co*-AAc) hydrogel synthesized by Hoffman and Dong¹⁶ permitted the release of drugs at pH 7.4 and showed release-off at



6.1 The diffusion of bioactive materials through stimuli-sensitive IPN hydrogels.

pH 1.4, and was proved to be a suitable carrier for indomethacin through the gastrointestinal (GI) tract.

In addition, electric current-sensitive hydrogels actuated by electric stimulus are particularly interesting in connection with the mechanical energy triggered by an electric signal.^{17–20} Electric current-sensitive hydrogels are usually made of polyelectrolytes and an insoluble but swellable polymer network which carries cations or anions. This system can transform chemical free energy directly into mechanical work to give isothermal energy conversion. A typical function of a gel containing ionic groups is to bend reversibly under the influence of an electric field, making it useful in some actuators driven by an electric field. From the viewpoint of mechanical engineering, great hopes are set on these materials as new actuators,^{17–20} especially in the fields of robotics and medical welfare instruments.

The present chapter will review the pH/temperature-sensitive properties of novel PVA/PAAC IPN hydrogels synthesized by a unique sequential method through UV irradiation and a freezing–thawing process.

6.2 Experimental

6.2.1 Materials

Acrylic acid monomer (AAc) obtained from Junsei Chemical Co. was purified by inhibitor remove column (Aldrich Chem. Co.) Poly(vinyl alcohol) (PVA; DP = 2500, degree of deacetylation = 99%) was purchased from Shinetsu Co. Methylenebisacrylamide (MBAAm) as a cross-linking agent and 2,2-dimethoxy-2-phenylacetophenone (DMPAP) as a photoinitiator were purchased from Aldrich Chem. Co. Indomethacin (anhydrous, MW = 357.8), used as a model drug, was obtained from Sigma Chem. Co. As five representative solutes, theophylline (99%, Aldrich Chem. Co.), vitamin B₁₂ (Sigma Chem. Co.), riboflavin (Junsei Chem. Co.), bovine serum albumin (Young Science Inc.) and cefazolin sodium were used. Cefazolin sodium was kindly donated by Chongkeundang R&D Center in Seoul, Korea.

6.2.2 Synthesis of PVA/PAAc IPN hydrogels

The PVA/PAAc IPNs were prepared by sequential method. PAAc as an initial network was synthesized inside a PVA solution using UV irradiation. PVA as a secondary network was then formed by repetitive freezing–thawing process. The whole reaction scheme of PVA/PAAc IPNs is described in Fig. 6.2. PVA was dissolved in deionized water and heated at 80 °C for 2 h to make 10 wt% aqueous solution. AAc monomers were mixed with 0.2 wt % DMPAP as a photoinitiator and 0.5 mol% MBAAm as a cross-linking agent. The mixture was combined with PVA solution to yield PVA–PAAc. The feed composition and designation of each sample are listed in Table 6.1.

The mixed solutions were poured onto Petri dishes and irradiated using a 450 W UV lamp (Ace Glass Co.) for 1 h under N₂ atmosphere. The irradiated samples were placed at – 50 °C for 6 h and at room temperature for 2 h. These freeze–thawing cycles were repeated eight times.

Table 6.1 Designation and feed contents of PVA/PAAc IPN

Sample name	PAAc (mol %)	AAc (g)	MBAAm (g)	DMPAP (g)
IPN37	70	5.70	0.061	0.0084
IPN46	60	4.89	0.052	0.0098
IPN55	50	3.26	0.035	0.0065
IPN64	40	2.16	0.023	0.0043
IPN73	30	1.62	0.017	0.0032

medium, as described elsewhere. The permeation studies were carried out using a two-chamber diffusion cell.

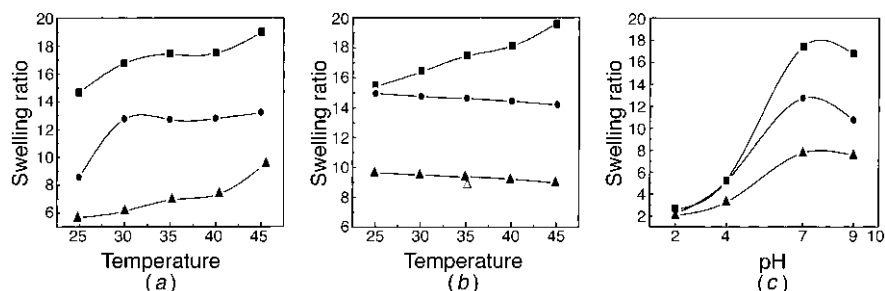
6.3 Results and discussion

6.3.1 Synthesis of PVA/PAAc IPNs

The sequential method by UV irradiation, followed by freezing and thawing, would be a novel method of preparing the stimuli-sensitive polymer hydrogel. The structure of the IPN samples prepared was confirmed by FTIR spectra.

6.3.2 Swelling measurement of PVA/PAAc IPNs

The swelling ratios of all PVA/PAAc IPNs were relatively high, and they showed reasonable sensitivity to both pH and temperature. Temperature-dependent swelling behaviours at pH 7 are shown in Fig. 6.3(a) and (b). Measurements were carried out with hydrogels after immersing the samples for 20 h at 25 °C. The IPN hydrogels showed different kinds of thermo-sensitivity. All IPN samples showed positive temperature-sensitive systems before reaching their equilibrated state as illustrated in Fig. 6.3(a). After equilibrium swelling, however, the swelling ratio of IPN46 increased with temperature, showing a positive temperature-sensitive system, while IPN64 and IPN55 exhibited negative temperature-sensitive systems. The swelling behaviours of IPN64 and IPN55 are similar to that of virgin PVA homopolymer.²² This is ascribable mainly to the swelling tendency of PVA itself, rather than to polymer–polymer interactions between PVA and PAAc, such as hydrogen bonding and ionic repulsion in PAAc. The PVA content, even in IPN55 hydrogels, is supposed to be greater than the PAAc content because the



6.3 Temperature/pH-dependent swelling behaviours of PVA–PAAc IPN: (a) temperature-dependent swelling behaviour before equilibrium (6 h) at 25 °C, (b) temperature-dependent swelling behaviour after equilibrium (24 h) at 25 °C, (c) pH-dependent swelling behaviours at 25 °C; (■) IPN 46, (●) IPN 55, (▲) IPN 64.

residual acrylic acid monomer, which did not take part in polymerization during the synthesis of the IPNs, was removed from the IPNs by washing after the whole procedure. Accordingly, the swelling changes in IPN46 must be related to the hydrogen bonding between two polymers and the ionic repulsion of carboxylate ion produced due to the breakage of hydrogen bondings, while those in IPN64 and IPN55 depend mainly on the swelling tendencies of PVA composition.

As shown in Fig. 6.3(c), pH-dependent swelling behaviour was observed at 35 °C with changes in pH. The pK_a value of PAAc is known to be 4.8.²¹ Therefore, at pH 2 and pH 4 buffer solutions, carboxyl groups in PAAc associate and form hydrogen bonding with PVA chains; thus, the swelling ratios are small. Carboxylate ions formed at pH greater than 4, however, induce the repulsion between them, and the hydrogen bondings between PVA and PAAc should decrease, resulting in the increase of free volume in the matrix and, therefore, a rapid increase in swelling ratios. The small deswelling that occurred at pH 9 is considered to be due to an increase of ionic strength in the buffer solution at pH 9, which might inhibit the polymer–water interactions inside the hydrogel matrix. The swelling ratio increased with the PAAc content within the PVA/PAAc IPNs.

The relationship between the changes in molecular structure in the IPN hydrogel and electrolytes in the buffer solution is shown in Table 6.2. The ionization of carboxylic acid in the IPN hydrogel was an important factor in the pH-dependent swelling. However, the interaction between ionic groups in the IPN chains and electrolytes in the buffer solution became more intense when the pH of the buffer solution changed from 4 to 7; therefore, when a pH was below the pK_a value of the PAAc (at pH 4) in which the carboxylic acid group in the IPN hydrogel was in a hydrogenated state, the effect of the ionic strength on the swelling was less than a pH above the pK_a value of PAAc (at pH 7) in which the carboxylic group in the IPN hydrogel was in an ionized state. For the buffer solution at pH 7, in which the ionic strength was adjusted to 0.01, the swelling ratio of each IPN sample became high, ranging from 15.2 to 33.4, while the increase of electrolyte concentration to 0.1 in the medium produced a drastic collapse of all the IPN hydrogels. However, the swelling of all IPN hydrogels at pH 4 was not dependent on ionic strength, as can be seen in Table 6.2.

6.3.3 Release experiment of drug from PVA/PAAc IPNs

All the samples exhibited higher release rates at higher temperatures. These results are in correspondence with the temperature-dependent swelling behaviours of PVA/PAAc IPN hydrogels. All IPN samples showed positive temperature-sensitive systems before they reached the equilibrated state. The

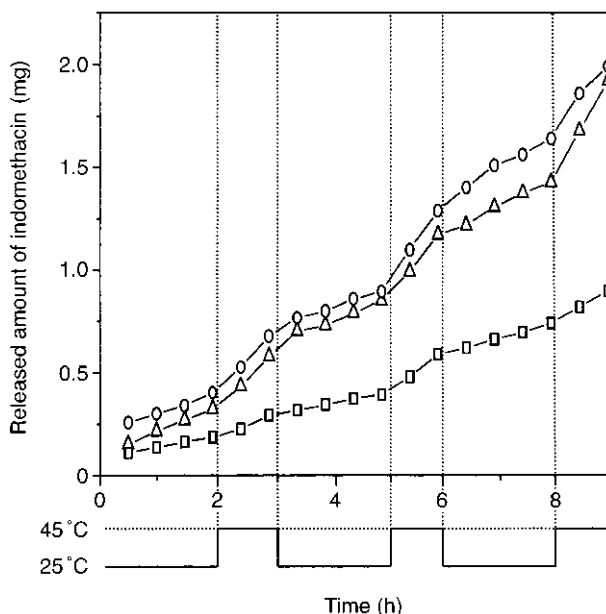
Table 6.2 Effect of pH and ionic strength in the swelling medium on the equilibrium swelling ratio of IPN hydrogels

Sample	pH	Ionic strength	Swelling ratio
IPN37	7	0.01	32.3 ± 0.92
IPN46	4	0.1	6.8 ± 0.44
		0.01	6.0 ± 0.91
		0.1	16.3 ± 1.80
IPN55	7	0.01	28.0 ± 0.36
		0.1	4.2 ± 0.47
		0.01	4.4 ± 0.30
IPN64	4	0.1	11.9 ± 1.80
		0.01	21.5 ± 1.50
		0.1	5.5 ± 1.32
IPN73	7	0.01	4.9 ± 1.20
		0.1	10.1 ± 0.67
		0.01	17.4 ± 0.58
IPN73	7	0.01	14.5 ± 1.13

release of the incorporated drugs within IPN hydrogels was delayed for about 10–15 hours, which was not enough time for all the samples to be fully equilibrated. The release profiles indicated positive temperature-sensitive release behaviours, and thus the composition of IPN was negligible in the temperature-dependent release system.

The changes of release rate for IPN46, IPN55, IPN64 hydrogels in response to stepwise temperature changes between 25 and 45 °C are shown in Fig. 6.4. High release rates are obtained at 45 °C, while low release rates are observed during the lower temperature period, as mentioned above. The released amounts from IPN46 and IPN55 are almost the same, while the released amount from IPN64 is small due to the low swelling. In the case of IPN64, the fact that the hydroxyl groups in PVA formed hydrogen bonding and had little chance to experience the ionic repulsion from carboxylate groups was proved.

The pH-sensitive release behaviours of indomethacin were observed at 25 °C with change in pH. Indomethacin is expected to diffuse through the water-swelling region in the polymer gel. At pH 4, PAAc is in the form of carboxylic acid, which produces hydrogen bonding with the hydroxyl group of PVA, resulting in the decrease of drug release. However, at pH 7, carboxylate ions formed in PAAc induced the drastic increase of swelling which exhibited high release rate. The release amounts from IPN46 and IPN55 were almost identical, and IPN64 gave lower values due to significant low swelling compared to the others at pH 4. It is considered that the release rate from IPN hydrogels is nearly independent of the composition of samples at pH 4. In the



6.4 Release change of indomethacin from IPN hydrogels in response to stepwise temperature change between 25 °C and 45 °C; (○) IPN46, (△) IPN55, (□) IPN64.

case of the drug release experiment at pH 7, more PAAc contents in IPN contributed to the higher release amount.

Oscillatory release profiles at 25 °C with changing pH levels between 4 and 7 are shown in Fig. 6.5. The plot gives the reversible change of release rate with pH fluctuation. IPN46 and IPN55 showed lower release at pH 4 and higher at pH 7, and continued reversible behaviour during the experiment. However, IPN64 did not show sharp reversible change because it did not have enough carboxylic groups.

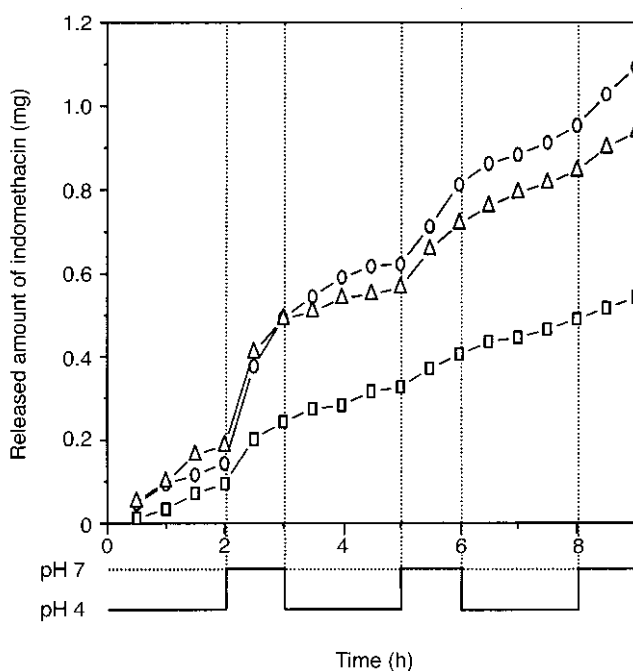
6.3.4 Solute permeation through PVA/PAAc IPNs

Solute permeation experiments were performed using five representative solutes with different molecular weights and hydrodynamic sizes. The characteristics of selected solutes are listed in Table 6.3. In the experimental buffer solution in which pH was adjusted to 4 or 7, theophylline,²³ vitamin B₁₂,²³ and BSA²³ were in a neutral state, and riboflavin²³ and cefazolin²⁴ showed ionized structures.

Table 6.4 shows the results of solute permeation experiment measured at 25 and 45 °C, respectively. The permeation of solutes through IPN hydrogels as a

Table 6.3 Characteristics of permeating solutes

Solutes	MW	Hydrodynamic radius (Å)	Ionic property at pH 7
Theophylline	180	3.5	Neutral
Riboflavin	376	5.8	Ionic
Cefazolin	476	6.5	Ionic
Vitamin B ₁₂	1355	8.5	Neutral
BSA	65 000	36.1	Neutral



6.5 Release change of indomethacin from IPN hydrogels in response to stepwise pH change between pH 4 and 7; (○) IPN46, (△) IPN55, (□) IPN64.

function of temperature was in accordance with the swelling behaviours of the IPNs. IPN46 exhibited a positive swelling change with temperature, as described in the swelling experiments. Therefore, all the solutes showed higher diffusion coefficients at high temperature. This is explained by the fact that the increase of diffusion coefficients at high temperature does not alter the interaction between solutes and IPN structure, but only causes an expansion

Table 6.4 The permeation studies of various solutes through IPN46 hydrogel at pH 7 buffer solution ($l=0.01$)

Solute	Temp. (°C)	P^a ($\times 10^6$ cm ² /s)	K_d^b	D^c ($\times 10^6$ cm ² /s)
Theophylline	25	7.63 ± 0.127	1.55 ± 0.035	4.94 ± 0.195
Riboflavin	25	0.99 ± 0.007	2.97 ± 0.028	0.33 ± 0.001
Cefazolin	25	0.42 ± 0.007	5.67 ± 0.064	0.07 ± 0.003
Vitamin B ₁₂	25	1.80 ± 0.099	1.20 ± 0.064	1.51 ± 0.163
BSA	25	1.03 ± 0.134	2.75 ± 0.043	0.41 ± 0.052
Theophylline	45	9.90 ± 0.141	0.81 ± 0.014	12.22 ± 0.039
Riboflavin	45	1.52 ± 0.028	2.35 ± 0.014	0.65 ± 0.016
Cefazolin	45	1.38 ± 0.092	9.14 ± 0.042	0.15 ± 0.011
Vitamin B ₁₂	45	4.06 ± 0.170	1.89 ± 0.099	2.15 ± 0.023
BSA	45	3.86 ± 0.134	4.74 ± 0.031	0.81 ± 0.034

^a P : permeability coefficient, ^b K_d : partition coefficient, ^c D : diffusion coefficient $n=3$ for each sample.

of IPN networks. Higher swelling in IPN at high temperature increases the free volume through which the solutes permeate more freely.

The partition coefficients (K_d) of solutes between hydrogel membranes and surrounding solutions are also shown in Table 6.4. The value of K_d is driven by interactions between the solutes and the polymer molecular structure. Due to the hydrophilicity of PVA/PAAc IPN hydrogels, it is predicted that more hydrophilic solutes are well distributed throughout the entire hydrogel membranes. As can be seen in Table 6.4, the K_d values of ionic solutes such as riboflavin and cefazolin are greater than those of non-ionic solutes, obviously due to induced ionic interaction between ionic solutes and the carboxylic acid group. BSA showed the largest K_d value among non-ionic solutes. This is believed to be caused by the protein adsorption to the polymer surfaces. However, further study is needed to verify the interaction, which affects and determines the partition coefficients of solutes within the swollen hydrogels.

The size of the solute was an important factor in determining the diffusion and thus permeation through IPN hydrogels. The hydrodynamic sizes of three solutes is in the range from 3.5 Å to 36.1 Å, as seen in Table 6.3. For non-ionic solutes which had no ionic interaction with ionizable hydrogel membranes, theophylline, having the smallest molecular size of 3.5 Å, showed the most rapid diffusion through the hydrogel. The diffusion of vitamin B₁₂ (hydrodynamic radius = 8.5 Å) was faster than that of BSA (hydrodynamic radius = 36.1 Å). The free volume caused by hydration may allow the pathway of solutes through which the larger molecules were excluded in the permeation. However, the diffusion of ionic solutes such as riboflavin and cefazolin were independent of their hydrodynamic size. Riboflavin and cefazolin, which are

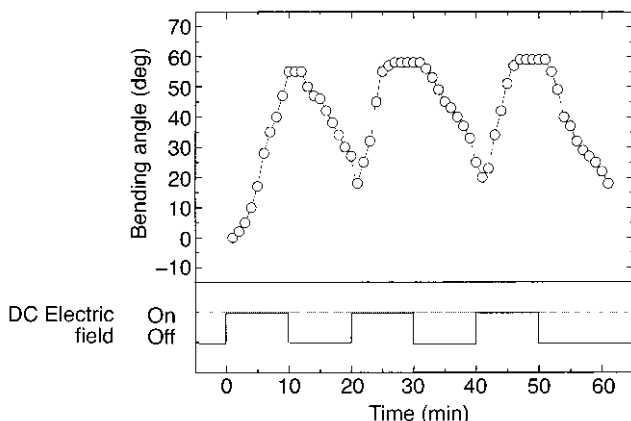
smaller in size than vitamin B₁₂ and BSA, gave a drastic reduction of diffusion coefficients. The permeability of solutes through IPN46 exhibited a similar tendency with diffusion coefficients. These results are indicative of the fact that, in the ionizable hydrogel membranes, the solute diffusion is much affected by solute size, as well as by ionic interaction between solutes and membranes.

6.3.5 Electro-responsive properties of PVA/PAAc IPNs

To investigate the electric-responsive behaviour of PVA/PAAc IPN hydrogel under electric stimulus, we measured the bending degree of IPN by varying several factors. When PVA/PAAc IPN hydrogel in NaCl electrolyte solution is subjected to an electric field, the IPN bends toward the anode. The gradient slope in the plot of the bending angle vs. time became steeper with increasing applied voltage, and then levelled off at steady state. Note that the equilibrium bending angle (EBA) and the bending speed increase with applied voltage. This could be explained by the fact that there was an enhancement in the transfer rate of the counter ions of the immobile carboxylate groups of PAAc within PVA/PAAc IPN from IPN to external solution and free ion moved from external solution into IPN, as the potential gradient in the electric field increased.

We investigated the effect of PAAc content on the EBA of IPN in 0.1 M NaCl solution at 10 V. As the content of the PAAc network increased, the EBA increased linearly. The bending speed also increased in proportion to the content of PAAc in the IPN. This may indicate that the EBA is not a rate-limiting step for bending in an equilibrated state.

In addition, the EBA and bending kinetics of IPN37 were measured in NaCl solution with different ionic strength. There was a critical ionic strength for the bending of PVA/PAAc IPN. The bending degree increased with ionic strength when the latter was less than 0.1, while it decreased at ionic strength of greater than 0.1. Furthermore, when the ionic strength of NaCl solution was 1.0, we could not observe the bending behaviour of PVA/PAAc IPN under the 10 V of applied voltage. As described above, an increase of electrolyte concentration in the solution induces the increase of free ions moving from the surrounding solution toward their counter electrode or into the IPN. As a result, the bending degree and speed of the IPN could increase. However, if the ionic strength of the solution is greater than a critical concentration, the shielding effect of polyions by the ions in the electrolytic solute occurred, leading to a reduction in the electrostatic repulsion of polyions and a decrease in the degree of bending. As already shown in Table 6.2, the swelling ratio of PVA/PAAc IPN in solution with the lower concentration of electrolyte (ionic strength = 0.01) was greater than that of higher electrolyte concentration (ionic strength = 0.1). Therefore, if it is compared with the bending results depending on the ionic



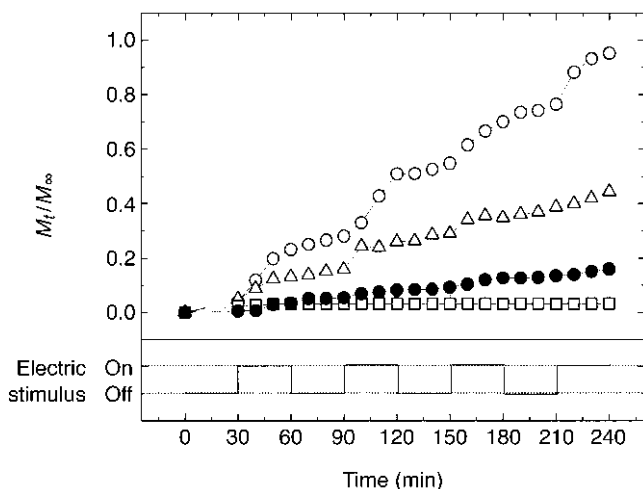
6.6 Reversible bending behaviour of IPN37 in NaCl solution (ionic strength=0.1) with changes in applied voltage 10 volts every 10 min.

strength of the solution, we could consider that the swelling of PVA/PAAc IPN by ionic strength does not significantly affect the bending behaviours of the IPN. In addition, stepwise bending behaviour of PVA/PAAc IPN depending on electric stimulus was observed for IPN in 0.1 M NaCl solution, with changes in the applied voltage of 10 V every 10 minutes. When the electric stimulus was removed, the IPN displaced to its original position. Also, if the polarity of the electric field was altered, IPN bent in the opposite direction. As shown in Fig. 6.6, PVA/PAAc IPN exhibited reversible bending behaviour according to the application of the electric field.

6.3.6 Drug release behaviour under electric fields

To investigate the electrically induced release behaviours of drugs, we determined the amount of released drug from PVA/PAAc IPN into a release medium under various conditions by UV-spectrophotometer. The drug-loaded IPN disk was placed between two carbon electrodes in a release chamber filled with a release medium. Applied voltage was then altered every 30 min.

Figure 6.7 exhibits the release behaviours of drugs from IPN37 as a function of time and the voltage of applied electric field in 0.9 wt % NaCl solution at 37 °C. The release behaviours of drugs from IPN37 as a function of time and the voltage of applied electric field in 0.9 wt % NaCl solution at 37 °C were investigated. Figure 6.7 shows the plot of M_t/M_∞ vs. time (min) while altering electric stimulus. Here, M_t is the amount of drug released up to time t , and M_∞ is the amount of drug present in the IPN at time $t = 0$. Depending on the electric stimulus being turned on and off, the release of drug molecules loaded

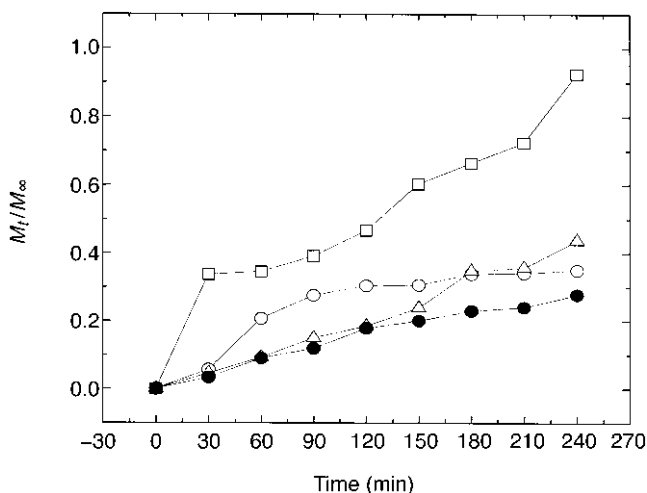


6.7 Release behaviours of cefazolin and theophylline from PVA-PAAC IPN55 as a function of applied voltage in 0.9% NaCl solution at 37 °C. Electric potential was altered every 30 min. —○— IPN55C, 10 V, —△— IPN55C, 5 V, —□— IPN55C, 0 V, —●— IPN55T, 5 V.

within PVA/PAAC IPN was switched on and off in a pulsatile fashion. A possible reason for this switching pattern of the release of drug molecules was that the electrically induced changes in osmotic pressure within the gel and local pH gradient attributed to water electrolysis could affect the swelling of IPN with charged groups.

In the case of theophylline (non-ionic solute), however, the magnitude of the ‘ON–OFF’ release pattern induced by the electrical stimulus was not so large as that of cefazolin (ionic solute). Particularly, the release rate of theophylline from IPN55T (theophylline-loaded IPN55) under 5 volts of electric potential was even smaller than that of cefazolin from IPN55C (cefazolin-loaded IPN55) without electric stimulus.

We conducted the release experiment of a drug from cefazolin- or theophylline-loaded IPN46 in NaCl solution with different ionic strength to examine the effect of the ionic strength of the release medium. Figure 6.8 shows the release behaviours of cefazolin and theophylline as a function of ionic strength in release medium at 5 V. In the case of IPN46C, the release rate of cefazolin increased in inverse proportion to the ionic strength of the release medium. Therefore, an increase of electrolyte concentration in the solution induces the movement of free ions from the surrounding solution toward their counter electrode or into IPN, resulting in an increase in release rate of cefazolin from charged PVA/PAAC IPN. The change of swelling in the PVA/PAAC IPN due to the ionic strength of the surrounding medium does not



6.8 Effect of ionic strength in release medium on release behaviours of cefazolin and theophylline from IPN46 under 5 V applied voltage. —○— IPN46C, 0.01 M NaCl, —△— IPN46C, 0.1 M NaCl, —□— IPN46C, 0.2 M NaCl, —●— IPN46T, 0.1 M NaCl.

significantly affect the release behaviours of the drug. It rather indicates that the electrically induced changes of osmotic pressure within the gel, the local pH gradient attributed to water electrolysis, and the squeezing effect of IPN gel were more important than the decrease of the swelling ratio due to the ionic strength of the release medium. However, in view of the ionic property of drugs, we can see that the release rate of ionic drugs is much faster than that of non-ionic drugs. An IPN46T sample containing a non-ionic drug, theophylline, exhibited a slower release rate in 0.1 M NaCl at 5 V than the ionic drug, cefazolin, in 0.01 M NaCl. This could be attributed to the enhancement of the release by electrophoresis of charged drug molecules.

6.4 Conclusions

PVA/PAAc IPNs with various compositions were prepared by a sequential synthetic method composed of UV polymerization and freeze–thawing process. A PVA/PAAc IPN exhibited different swelling patterns as a function of pH, temperature, ionic strength of external solution, and the content of ionic group in IPN. The release of indomethacin from these IPN hydrogels was dominated by the magnitude of swelling in the IPN hydrogels. In the temperature-sensitive system, the positive release of drugs caused by the hydrogen bonding between PVA and PAAc was observed, showing an increase of the released amount with higher temperature. In the case of

pH-dependent release, changing the pH controlled the release rate. At pH 7, higher release amounts were observed, since the water contents after swelling increased significantly. The permeability of non-ionic solutes changed according to the variation in swelling in the IPN hydrogel. Smaller solutes and higher swelling of the IPN hydrogel produced higher diffusion coefficients. However, the permeability of ionic solutes at pH 7 through IPN decreased, while the swelling of the IPN hydrogel increased. When a swollen PVA/PAAc IPN was placed between a pair of electrodes, the IPN exhibited bending behaviours upon the application of an electric field. The release behaviours of drug molecules from negatively charged PVA/PAAc IPN were switched on and off in a pulsatile pattern depending on the applied electrical stimulus. The release amount and the release rate of the drug were influenced by the applied voltage, the ionic group contents of the IPN, the ionic properties of the drug, and the ionic strength of the release medium. Therefore, the present IPN system was valid in pH/temperature/electrical-responsive drug delivery.

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