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Synthesis and characterization of semi-interpenetrating polymer networks using biocompatible polyurethane and acrylamide monomer

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ABSTRACT

Semi-interpenetrating polymer networks (semi-IPNs) of acrylamide based polyurethanes were synthesized from different NCO-terminated polyurethane prepolymers derived from polytetramethylene ether glycol (PTMEG). The resulting semi-IPNs were characterized using FTIR, DSC, and TGA measurements. Variation in the NCO/OH ratio and the molecular weight of the diol gave semi-IPNs with different types of mechanical characteristics varying from elastomer to brittle plastic properties. Differential scanning calorimetry (DSC) data revealed a difference in the glass transition temperature (T_g) of the semi-IPNs relative to the normal polyacrylamide (PAAM) network. Incorporation of polyurethane into polyacrylamide network in the form of an interpenetrating polymer networks enhanced the mechanical and thermal properties of the semi-IPNs due to higher crosslink density imparted by the hard segment content. The swelling behavior of both the semi-IPNs and the individual polyacrylamide (PAAM) network in different pH conditions were investigated to check their biocompatibility and possible usage in biomedical field. The hydrolytic stability of the semi-IPNs and the polyacrylamide (PAMM) network was studied using phosphate buffer solution. The hydrolytic stability of the semi-IPNs was found to be more compared to PAMM network. The morphology of both the semi-IPNs and the individual polyacrylamide (PAAM) network was investigated using SEM.

1. Introduction

An increasing number of polymeric materials are made from polymer blends. Most of them are phase separated as polymer pairs are generally immiscible. In the last few years, research has been oriented towards developing modified systems which exhibit enhanced miscibility. Polymer compatibility can be improved through the establishment of physical and/or chemical interactions between components. One approach to do this is to combine polymers in interpenetrating polymer network (IPN) form. Crosslinking, mutual chain entanglement and eventual internetwork grafting [1–4] in interpenetrating polymer networks (IPNs) produce finer dispersion of one polymer into the other. IPNs could help to improve the mechanical strength and resiliency of the polymer due to physical entanglements and network interactions when compared to individual crosslinked networks [4–8].

Polymeric hydrogels in the form of interpenetrating polymer networks (IPNs) are able to absorb large amounts of water without dissolving. They have been proposed for many biomedical applications due to their good biocompatibility and water permeation properties [9]. Polymeric hydrogels are promising candidates for tissue engineering matrices due to the fact that the hydrophilic nature and mechanical properties of bulk polymeric hydrogels resemble those of soft tissues [10–12]. Mechanical properties of the polyacrylamide gels in their swollen state are generally feeble and reinforcement is often desired. The mechanical strength of polyacrylamide gel has been enhanced by incorporation of 10% of polyurethane in the form of interpenetrating polymer network [13–15]. Block copolymerization of N-isopropylacrylamide (NIPAM) with

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polyurethane in terms of AB crosslinked polymers were carried out [16]. Polyurethanes have proved to be potential material for biomedical applications because of their high mechanical strength, flexibility, fatigue resistance and biocompatible nature [17–22]. The swelling ratio of a hydrogel depends on its network structure, which is monitored by the conditions of the crosslinking polymerization or by incorporating a more hydrophilic comonomer into the network structures [23–28].

This article deals with the synthesis of NCO-terminated polyurethane prepolymer incorporated acrylamide based semi-IPNs. The mechanical, thermal and swelling characteristics of the resultant semi-IPNs have been investigated. Results revealed enhanced mechanical and thermal properties of polyurethane incorporated semi-IPN when compared to individual polyacrylamide network (PAAM). Enhanced hydrolytic stability was achieved through the incorporation of NCO-terminated polyurethane prepolymer into the polyacrylamide network. The swelling properties of both the semi-IPNs and polyacrylamide network varied with different pH conditions.

2. Experimental

2.1. Materials

The raw materials polytetramethyleneether glyol (PTMEG, $M_n = 1000, 2000$) polyols having viscosities in the range of 1000–2000 cps at 70 °C were obtained as commercial grade chemicals from BASF. The polyol PTMEG was degassed at 70 °C for 3 h. 1,4-Butanediol (BDO) was purchased from Aldrich. Toluene diisocyanate (TDI) was used as received from Huntsmann. N,N′-Methylenebisacrylamide (MBAAM), acrylamide (AAM), benzoyl peroxide (BPO), potassium per sulphate ($K_2S_2O_8$) and dibutyltindilaurate (DBTDL) were purchased from Merck Chemicals Co. Tetrahydrofuran (THF) purchased from Merck Chemicals Co. was distilled at a temperature of 60–70 °C prior to use.

2.2. Preparation of polyacrylamide network (PAAM)

Acrylamide monomer (AAM) (5.602×10^{-3} mole) and N,N′-methylenebisacrylamide (MBAAM) (6.486×10^{-4} mole) were dissolved in 2 ml of deionised water and 1 ml of potassium per sulphate solution was added and the solution was aspirated for 15 min to remove dissolved oxygen. Polymerization was carried out in a constant temperature bath at 55 °C for 30 min. The crosslinked polyacrylamide gel obtained was washed with distilled water to remove unreacted monomer and residual initiator by immersing the gel in deionised water for 24 h. The yield of the crosslinked gel was found to be 94%.

2.3. Preparation of NCO-terminated polyurethane prepolymer (PTMEU-PP)

In the preparation of NCO-terminated polyurethane prepolymer varying NCO/OH ratio of toluene diisocyanate (TDI) and polytetramethyleneether glycol (PTMEG) of molecular weight 1000 were added slowly with stirring in a three necked flask equipped with a mechanical stirrer and a very small amount of catalyst DBTDL was added and 1,4-butanediol (BDO) was added for chain extension and the reaction was carried out at 40 °C for 2 h by purging nitrogen gas. The completion of the reaction was determined by the di-*n*-butylamine titration method when the isocyanate group content of the reaction mixture reached the theoretical value. This was also confirmed through a characteristic absorption peak at 2270 cm^{-1} for NCO group. The same procedure was carried out for the preparation of NCO-terminated polyurethane prepolymer by varying the NCO/OH ratio of toulene diisocyanate (TDI) and polytetramethyleneether glycol (PTMEG) of molecular weight 2000. The yield of PTEMU-PP1000 and PTEMU-PP2000 was found to be 97% and 98%, respectively.

2.4. Preparation of semi-interpenetrating polymer networks of poly(acrylamide) and polyurethane prepolymer (PTMEU-PP/PAAM) semi-IPNs

Semi-IPNs were synthesized by charging the polyurethane prepolymer in different proportions into a round-bottomed flask. To this, the mixture of acrylamide (AAM), N,N′-methylenebisacrylamide (MBAMM) (0.01%w/w) and BPO (0.5%w/w) was added and 20 wt% of THF was added. The mixture was stirred at room temperature for 15 min to form a homogeneous solution. The temperature was then increased to 70 °C to initiate acrylamide polymerization. After stirring for 1 h, the viscous solution was degassed to remove trapped bubbles and poured into a glass mould kept in a preheated oven maintained at 60 °C. It was kept at this temperature for 24 h and at 100 °C for 2 h to facilitate the complete network formation. The film thus formed was cooled slowly and removed from the mould and the dried films were used for further studies. The yield of PTEMU-PP1000/PAAM semi-IPN and PTEMU-PP2000 PAAM semi-IPN was found to be 95% and 96%, respectively.

2.5. Characterization

Fourier transform infrared (FTIR) spectra were obtained by using a KBr pellet on a spectrum one FTIR (Perkin-Elmer Instruments, USA) in the wave number range 4000–400 cm^{-1}.

Differential scanning calorimetry (DSC) thermograms were obtained using a DSC 200PC NETZSCH-Geratebau GmbH thermal analyzer. The heating rate was 20 °C min^{-1} in the temperature range of −150 to 300 °C.

The weight loss of thermo gravimetric analysis (TGA) was performed on a STA409PC NETZSCH-Geratebau GmbH thermal analyzer in nitrogen atmosphere at a heating rate of 20 °C min^{-1}.

The water absorption of PAAM and the semi-IPN films was determined by immersing the cut PAAM and semi-IPN membranes in a beaker of water at 37 °C. The membranes with a thickness of 1 mm was cut into circular disks of 20 mm diameter by using a sharp-edged stainless steel knife. The samples were weighed every 10 min until they attained the maximum water content. The water absorption (WS) of the semi-IPNs was calculated by

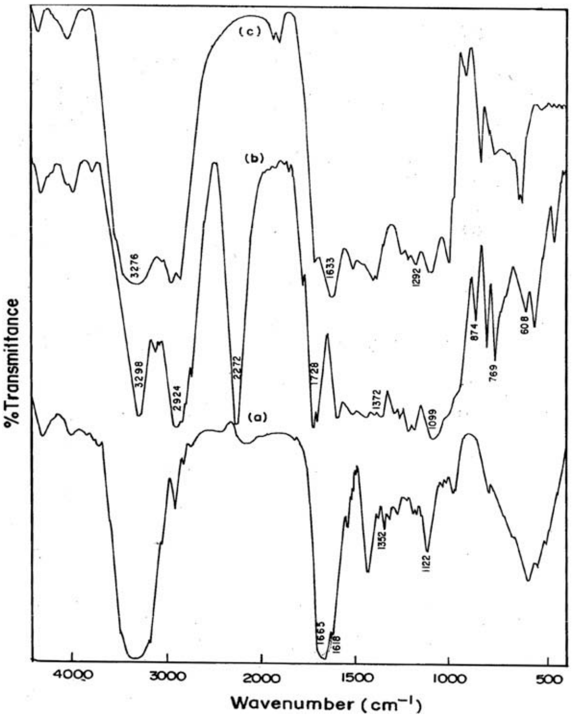

Fig. 1. FTIR spectra of (a) PAAM, (b) polyurethane prepolymer (PTMEU-PP1000) and (c) (PTMEU-PP1000/PAAM) semi-IPN.

$$\mathrm{WS} = [W_s - W_d/W_d] \times 100$$

where W_s and W_d are the weights of the water absorbed and the dry samples, respectively.

The hydrolytic stability was determined as follows: 12 preweighed dry films were saturated with phosphate buffer solution (pH 7.4) and stored in sealed glass vials and stored in an oven at 80 °C. Three samples were removed after 3, 5, 7 and 14 days, respectively. They were washed with distilled water and dried at 80 °C for 16 h. The percent weight loss of sample after different periods of testing were obtained by comparing the weight of dry sample before and after testing.

Tensile strength and percentage elongation of the samples were measured on a universal testing machine at a crosshead speed of 5 mm min^{-1}. Both dried and swollen samples were measured; the tensile test specimen, 1 mm thick and 6 mm wide were cut from the sheet.

Phase morphology was examined by a Leo stereoscan 440 scanning electron microscopy. The samples were fractured in liquid nitrogen in order to preserve the sample morphology, and sputter-coated with gold prior to being viewed under the microscope.

3. Results and discussion

3.1. FTIR analysis

The FTIR spectra of NCO-terminated polyurethane prepolymer (PTEMU-PP1000) and polyurethane incorporated polyacrylamide semi-interpenetrating polymer networks (PTMEU-PP1000-20/PAMM-80) semi-IPN were shown in Fig. 1b and c. The FTIR spectra of polyurethane prepolymer showed characteristic absorption bands at 1728 and 3298 cm^{-1} corresponding to C=O group of urethane linkage and N—H stretching of urethane amide. As the prepolymer is isocyanate terminated, an intense sharp absorption band for NCO group was observed at 2270 cm^{-1}. The FTIR spectra of PTMEU-PP1000-20/PAMM-80 semi-IPN showed no characteristic absorption band at 2270 cm^{-1} confirmed the grafting and interpenetration of acrylamide with NCO-terminated polyurethane prepolymer. The presence of urea group was observed around 1510–1633 cm^{-1}. The peak around 1630–1650 cm^{-1} and a weak band around 1292–1330 cm^{-1} corresponds to C=O, N—H bending and C—N stretching of $\mathrm{CONH_2}$ group of polyacrylamide. The FTIR spectrum of individual polyacrylamide network was shown in Fig. 1a. In the polyacrylamide (PAAM) network spectrum the strong absorption at 3435 $\mathrm{cm}^{-1}$and the shoulder at around 3200 cm^{-1} are attributed to the N—H stretching vibrations of the primary amide. The crosslinked polyacrylamide exhibit the characteristic absorption peaks of polyacrylamides; 1655–1665 cm^{-1} (strong), 1618 cm^{-1} (weak) and 1352 cm^{-1} (weak), indicating the C=O, N—H bending and C—N stretching, respectively, which are the $\mathrm{CONH_2}$ group.

3.2. Thermal properties

The thermal behavior of polyacrylamide (PAAM) and polyurethane incorporated polyacrylamide interpenetrating polymer networks (PTMEU-PP/PAMM) semi-IPNs was examined by TGA and DSC. The numerical data are presented in Table 1.

The TGA thermograms of PAAM network and low and high molecular weight based semi-IPNs (i.e.) PTMEU-PP1000/PAAM semi-IPN and PTMEU-PP2000/PAAM semi-IPNs were shown in Fig. 2a and c. On the basis of thermogravimetric analysis data obtained, it was found be that both the PTMEU-PP1000/PAAM semi-IPN and PTMEU-PP2000/PAAM semi-IPNs showed two stages of decomposition; the first stage decomposition was due to the degradation of PAAM that is due to loss of ammonia with the formation of imide group via cyclisation. Second stage decomposition may be due to decrosslinking of two networks structures. The

Table 1
TGA, DSC thermogram data for PAAM, PTMEU-PP1000/PAAM semi-IPN and PTMEU-PP2000/PAAM semi-IPN.

Sample code	Stages of decomposition			T_g/T_m (°C)
	I (°C)	II (°C)	III (°C)	
PAAM	180–210	284–314	381–425	88–90, 110
PTMEU-PP1000/PAMM semi-IPN	120–257	250–450	–	−43, 66.2
PTMEU-PP2000/PAMM semi-IPN	250–380	390–490	–	−53, 94

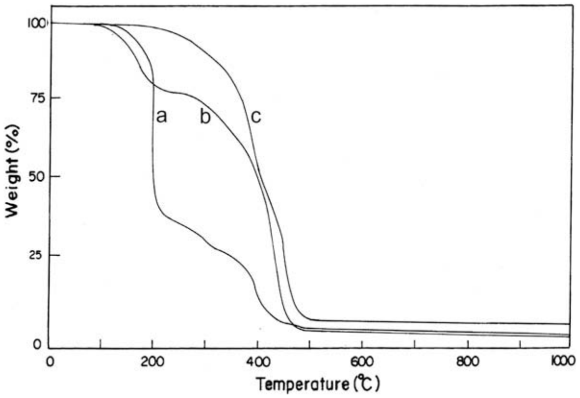

Fig. 2. TGA thermogram of (a) PAAM, (b) PTMEU-PP1000/PAAM semi-IPN and (c) PTMEU-PP2000/PAAM semi-IPN.

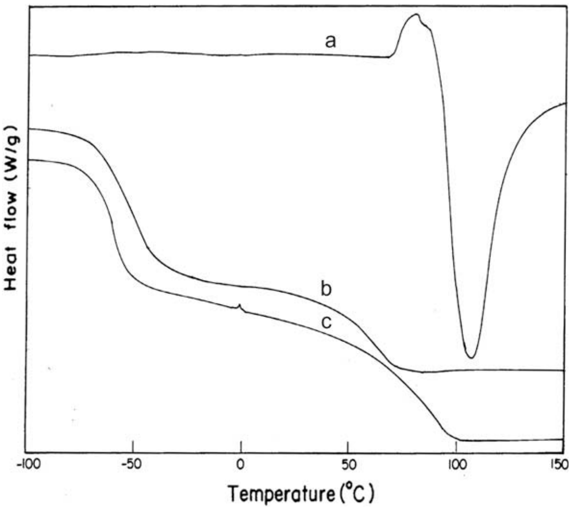

Fig. 3. DSC thermogram of (a) PAAM, (b) PTMEU-PP1000/PAAM semi-IPN and (c) PTMEU-PP2000/PAAM semi-IPN.

PTMEU-PP2000/PAAM semi-IPN showed better thermal stability than PTMEU-PP1000/PAAM semi-IPN. In the case of PAAM network three stages of decomposition was seen, the weight loss above 210 °C was due to the degradation of PAAM that is due to loss of ammonia with the formation of imide group via cyclisation [29]. The degradation of volatile products such as water and ammonia was observed below 320 °C. Decomposition of cyclised product was observed starting from 381 °C.

The DSC thermograms of PAAM network and low and high molecular weight based semi-IPNs (i.e.) PTMEU-PP1000/PAAM semi-IPN and PTMEU-PP2000/PAAM semi-IPNs were shown in Fig. 3a and c and their phase transition temperature were listed in Table 1.

The DSC thermogram of both semi-IPNs (PTMEU-PP1000/PAAM semi-IPN and PTMEU-PP2000/PAAM semi-IPN) showed double T_g's corresponding to T_g of PU (lower one) and T_g of PAAM (higher one) based on the point of inflection. The T_g of PTMEU-PP2000/PAAM semi-IPN was lower compared to PTMEU-PP1000/PAAM semi-IPN due to increased chain length in PTMEU-PP2000/PAAM semi-IPN because the higher length of the curing agent the longer distance between the network junctions formed. The T_g of PAAM was higher in PTMEU-PP2000/PAAM semi-IPN when compared to PTMEU-PP1000/PAAM semi-IPN due to increased crosslinking between polyurethane and acrylamide monomer in high molecular weight polymer. The T_g of PAAM was higher due to the increased crosslink density in the network.

3.3. Swelling properties

The swelling data's of PAAM network and the semi-IPNs were given in Table 2. The swelling behaviors of the semi-IPNs were found to decrease when compared to PAMM this may be due to the increased crosslink density in the IPNs and also due to the interpenetration of the networks. The swelling ratio of high molecular weight semi-IPN was higher when compared to lower molecular weight semi-IPN. This was due to the looser network of the high molecular weight semi-IPN induced by the flexibility of the high molecular weight PTMEG soft segment. Another reason for the observed decrease in the swelling ratio may be that with increasing hydrophilic segments in the semi-IPNs the polymer volume fraction decreases which reduces the mesh sizes of the free volumes. The mesh size characterize the space between the macromolecular chains. Obviously, a decrease in mesh size will result in a penetration of less number of water molecules into the network.

The effect of pH in regulating water sorption of polymeric IPNs is of greater significance as a change in pH of the swelling medium often results in a fluctuation in free volumes accessible to penetrate water molecules which, in turn affects swelling characteristics of the semi-IPNs. In the present investigation in both acidic pH 4 and basic pH 9 were carried out and the results are depicted in Table 2. It was found that the equilibrium swelling increases in pH 9 but decreases in pH 4 this is due to the fact that at increased pH the acrylamide undergo partial hydrolysis and

Table 2
Swelling and hydrolytic stability data for PAAM, PTMEU-PP1000/PAAM semi-IPN and PTMEU-PP2000/PAAM semi-IPN.

Sample code	Equilibrium swelling ratio (%)	Equilibrium swelling ratio at different pH		Percentage weight loss (%)			
		4	9	Days			
				3	5	7	14
PAAM	406	352	412	320	316	312	310
PTMEU-PP1000/PAMM semi-IPN	310	316	354	342	340	339	338
PTMEU-PP2000/PAMM semi-IPN	360	362	402	391	389	384	384

Table 3
Mechanical properties of PAAM, PTMEU-PP1000/PAAM semi-IPN and PTMEU-PP2000/PAAM semi-IPN.

Sample code	NCO/OH ratio	PTMEU-PP (mole %)	PAMM (mole %)	Ultimate tensile strength (kg/cm^2)		% Elongation at break	
				Dry state	Swollen state	Dry state	Swollen state
PAMM	–	–	100	Brittle	3.3	110	140
PTMEU-PP1000/PAMM semi-IPN	2.2	20	80	15	11	240	280
PTMEU-PP2000/PAMM semi-IPN	2.4	20	80	19	13	300	360

produce anionic charged centers along the co-polymeric chains and cause repulsions between the macromolecular chains and free volume widen in the semi-IPNs resulting in enhanced water absorption.

The hydrolytic stability is an important property in determining the suitability of the biomaterial for use in medical devices. Hydrolytic stability is a measure of susceptibility to degradation during thermal disinfection and shelf life. The stability was demonstrated by the weight loss of the dry sample as well as the change in water content for the samples. The hydrolytic stability data of both PAAM network and semi-IPNs (PTMEU-PP1000/PAAM semi-IPN and PTMEU-PP2000/PAAM semi-IPN) were given in Table 2. From the percentage weight loss data it was found that the hydrolytic stability of both the semi-IPNs was better compared to the PAAM network. In the case of PAAM network increased hydrolysis of the network resulted as the basic medium increased, whereas in the case semi-IPNs the hydrolysis of the semi-IPNs decreased due to enhanced crosslinking as a result the percentage weight loss also decreased. The shrinkage of the network was not found even at elevated temperature which clearly indicated the stability of the network in the form of interpenetrating network.

3.4. Mechanical properties

The effects of biomaterial composition on the mechanical properties as determined using tensile analysis were shown in Table 3. The mechanical studies data of the semi-IPNs showed improved tensile and elongation properties when compared to PAMM network. The incorporation of polyurethane prepolymer (PTMEU-PP) by varying the NCO/OH ratio with the acrylamide (AMM) monomer improved the tensile and elongation properties. The 20/80 ratio (wt%) showed improved tensile and elongation properties. Moreover as the NCO/OH content of the polyurethane prepolymer increases the tensile strength of the semi-IPNs increased. This may be due to higher crosslink density imparted by the hard segment content and also due to the interpenetration of the networks. The high molecular weight semi-IPN showed higher elongation properties compared to low molecular weight semi-IPN. This may be due to the higher flexibility imparted by high molecular weight PTMEG soft segment than the low molecular weight PTMEG soft segment. The tensile strength of the swollen network was less compared to dried gel because of the fact that water molecules imbibed in the network reduces the tensile strength of the semi-IPN network. This phenomenon was reverse in the case of percentage elongation for the semi-IPNs since the elongation is enhanced in the swollen state due to reduced water sorption persisting in the network due to the interpenetration of the network structures. The highest mechanical strength of the semi-IPNs is due its chain distribution and molecular noncovalent interaction which resulted from the entanglement of the network structures.

3.5. SEM analysis

Fig. 4a and b shows the morphology of dry PAAM network and PTMEU-PP1000/PAAM semi-IPN. Both the structures were found to be porous with a fractured surface. In the case of PTMEU-PP1000/PAAM semi-IPN a cell like structure with the particles of polyacrylamide dispersed on it was observed. The structure of PTMEU-PP1000/PAAM semi-IPN was entirely different from PAMM structure which clearly indicates that the interpenetration of acrylamide on to polyurethane network has taken place.

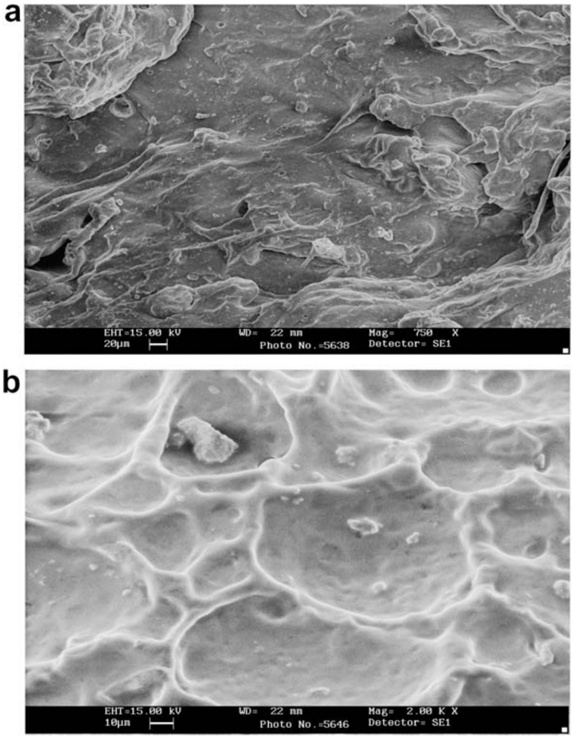

Fig. 4. SEM image of (a) PAAM network and (b) PTMEU-PP1000/PAAM semi-IPN.

The scarcity in the pore volume in the semi-IPN structure revealed the increased crosslink density in the network structure of semi-IPN due to interpenetration.

4. Conclusions

Interpenetrating polymer networks prepared from acrylamide and different NCO-terminated polyurethane prepolymer (PTMEU-PP) showed better thermal stability, compatibility, tensile and elongation properties compared to the individual polyacrylamide network. The low T_g values and soft characteristics of polyurethane within the semi-IPN network demonstrated the flexibility of the semi-IPN structure when compared to pure polyacrylamide network. Morphological observations using the scanning electron microscope revealed the compatibility of the interpenetrating polymer networks. The swelling properties of both the semi-IPNs decreased by the incorporation of the NCO-terminated polyurethane prepolymer. The swelling properties of the semi-IPNs decreased at acidic pH while a reverse trend was seen in basic pH. The semi-IPNs were found to be hydrolytically stable in phosphate buffer solution. Hence it can be concluded that PTMEG based semi-IPNs can be used as a potential material for biomedical applications.

References

[1] Yu-chin Lai, Louis Baccei. Novel polyurethane hydrogels for biomedical applications. J Appl Polym Sci 1995;56:301–10.

[2] Shan-Yang Lin, Ko-Shao Chen, Liang Run-chu. Design and evaluation of drug loaded wound dressing having thermoresponsive, adhesive, absorptive and easy peeling properties. Biomaterials 2001;22:2999–3004.

[3] Nevissas V, Widmaier JM, Meyer GC. Effect of crosslink density and internetwork grafting on the transparency of polyurethane/polystyrene interpenetrating polymer networks. J Appl Polym Sci 1988;36:1467–73.

[4] Widmaier JM, Chenal JM. Investigations of miscibility in interpenetrated systems of polyurethane and polystyrene obtained at room temperature. Macromol Symp 2004;216:179–88.

[5] Sperling LH. IPNs and related materials. New York: Plenum; 1981. Chapter 5.

[6] Kim SJ, Kim SI. Thermal characterization of chitosan and polyacrylamide semi-interpenetrating polymer networks. High Perform Polym 2002;14:309–16.

[7] Chivukula P, Dosek K. Synthesis and characterization of novel aromatic azo bond-containing IPN hydrogels. Biomaterials 2006;27:1140–51.

[8] Muniz EC, Geuskens G. Polyacrylamide hydrogels and semi-IPNs with poly (N-isopropylacrylamide): mechanical properties by measure of compressive elastic modulus. J Mater Sci Mater Med 2001;12:879–81.

[9] Peppas NA, Hilt J, Khademhosseini A, Langer R. Hydrogels in biology and medicine: From molecular principles to bionanotechnology. Adv mater 2006;18:1345–60.

[10] Ke-Jun Yao, Wen-Jing Zhou. Synthesis and water absorbency of the copolymer of acrylamide with anionic monomers. J Appl Polym Sci 1994;53:1533–8.

[11] Lim YH, Kim D, Lee DS. Drug releasing characteristics of thermo and pH-sensitive interpenetrating polymer networks based on poly (N-isopropylacrylamide). J Appl Polym Sci 1997;64:2647–55.

[12] Hitoshi Kubota, Akira Fukuda. Photopolymerization synthesis of poly (N-isopropylacrylamide) hydrogels. J Appl Polym Sci 1997;65:1313–8.

[13] Yong Qiu, Kinam Park. Superporous IPN hydrogels having enhanced mechanical properties. AAPS PharmSciTech 2003;4:406–12.

[14] Baek SH, Kim BK. Synthesis of polyacrylamide/polyurethane hydrogels by latex IPN and AB crosslinked polymers. Colloids Surf A Physicochem Eng Aspects 2003;220:191–8.

[15] Prabha Nair D, Jabalan M. Polyurethane –polyacrylamide IPNs. I. synthesis and characterization. J Polym Sci A Polym Chem 1990;28:3775–86.

[16] Park CW, Cho SM, Kim BK. Synthesis and properties of thermosensitive polyurethane–b-poly (N-isopropylacrylamide). React Func polym 2006;66:585–91.

[17] Liu CJ, Hsieh KH, Ho KS, Hsieh TT. 2-Hydroxyethylmethacrylate-terminated polyurethane/polyurethane IPNs. J Biomed Mater Res 1997;34:261–8.

[18] Petrini P, Fare S, Piva A, Tanzi MC. Design, synthesis and properties of polyurethane hydrogels for tissue engineering. J Mater Sci Mater Med 2003;14:683–6.

[19] Pennings AT, Knol KE, Hoppen HJ. A two-ply artificial blood vessel of polyurethane and poly (L-lactide). Colloid Polym Sci 1990;268:2–11.

[20] David Jones S, David McLaughlin WJ, Colin Mc Coy P, Sean German P. Physiochemical characterization and biological evaluation of hydrogel-(ϵ-caprolactone) IPNs as novel urinary biomaterials. Biomaterials 2005;26:1761–70.

[21] Dror M, Elsaber MZ, Berry GC. Gradient interpenetrating polymer networks. I. Poly (ether urethane) and polyacrylamide IPN. J Appl Polym Sci 2003;26:1741–57.

[22] Fangxing LI, Ju Zuo, Limer Dong, Hong Jun Wang. Study on the synthesis of high elongation polyurethane. Eur Polym J 1998;34:59–66.

[23] Hiroki Katono, Atushi Maruyarma. Thermo-responsive swelling and drug release switching of interpenetrating polymer networks composed of poly (acrylamide-co-butylmethacrylate) and poly (acrylic acid). J Control Release 1991;16:215–28.

[24] Gomez Anton MR, Rodriguez JG, Pierola IF. Polymer effects in proton-transfer reaction poly (2-vinyl quinoline). Macromolecules 1986;19:2932–6.

[25] Tuncer Caykara, Ilkay Akcakaya. Synthesis and network structure of ionic poly (N,N′-dimethylacrylamide-co-acrylamide) hydrogels: comparison of swelling degree with theory. Eur Polym J 2006;42:1437–45.

[26] Sen M, Guven O. Prediction of swelling behavior of hydrogels containing diprotic acid moieties. Polymer 1998;39:1165–72.

[27] Xue W, Champ S, Huglin MB. New superabsorbent thermoreversible hydrogels. Polymer 2001;42:2247–50.

[28] Zeng You, Wang Rui-Chun, Gu Ya-Xin, Liu Yun-Xue, Zhao Jin-Bo. Effect of elastic polyurethane on swelling/deswelling behavior of polyacrylamide hydrogels. Ziran kexueban 2004;20:192–5.

[29] Nayak BR, Singh RP. Development of graft copolymer flocculating agents based on hydroxy propyl guar gum and acrylamide. J Appl Polym Sci 2001;81:1776–85.