

NANO-TiO₂ *IN-SITU* HYBRID POLYURETHANE WITH ENHANCED PERMEABILITY FOR PU LEATHER MANUFACTURE

by

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ABSTRACT

A novel organic-inorganic nano-hybrid process combined with industrialized wet-phase inversion coating-forming method was developed for the modification of polyurethane (PU) leather coating with *in-situ*-generated nano-TiO₂. The cross section morphologies, water vapor permeability, gas permeability, mesopore size distribution and specific surface area of the hybrid samples were investigated. SEM analysis indicated that when the TiO₂ concentration increased from 0.25wt% to 1.00wt%, the average size of nano particles, which dispersed uniformly throughout the polymer matrix, increased correspondingly from 60-80nm to 90-120nm without obvious agglomerates observed. After nano hybridization, both water vapor and gas (hydrogen, nitrogen and oxygen) permeability of samples were found to increase with an increasing concentration of nano-TiO₂, which was explained as voids formed at the polymer-nano particle interface due to phase incompatibility. The existence of such voids in samples was proven in the nitrogen adsorption/desorption experiment, by the detection of extra mesopores and higher specific surface area than predicted values. With industrial applicability in the manufacture of PU synthetic leather, the wet-phase inversion hybrid process developed in this study may be of great potential for improving the wear comfort of PU coated leather products.

RESUME

Un novedoso proceso nano-híbrido, orgánico-inorgánico, combinado con un método industrializado de recubrimiento por inversión en fase húmeda fue desarrollado para la modificación de cueros con recubrimiento de poliuretano (PU) con nano-TiO₂ generado *in situ*. La morfología de la sección transversal, permeabilidad al vapor de agua, permeabilidad al gas, la distribución y tamaño del mesoporo y el área específica de las muestras híbridas se investigaron. El análisis mediante SEM indica que cuando la concentración de TiO₂ aumenta de 0.25% a 1.00%, el tamaño medio de las nano partículas, dispersas de manera uniforme en toda la matriz polimérica, se incrementa correspondientemente de 60-80nm a 90-120nm sin que se observen aglomerados evidentes. Después de la nano hibridación, tanto el vapor de agua y la permeabilidad al gas (hidrógeno, nitrógeno y oxígeno) de las muestras se encontraron con una creciente concentración de nano-TiO₂, que fue explicada como huecos formados en la interface de la nano-partícula del polímero debido a la incompatibilidad de fase. La existencia de dichos huecos en las muestras se demostró en la prueba de adsorción/desorción del nitrógeno, por la detección extra de mesoporos y una mayor área de superficie específica que los valores previstos. Con la aplicación industrial en la fabricación de cuero sintético de PU, el proceso híbrido de inversión en fase húmeda desarrollado en este estudio puede ser de gran potencial para mejorar el confort de los productos de cuero recubiertos con PU.

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This work is presented because the technology, including the use novel “fillers,” may be of interest in the filed of leather coatings.

INTRODUCTION

During the past decades, worldwide demand for leather kept escalating as living standards rose, which, considering the acute shortage of raw hides and skins with a constant upward pressure on price, aroused researchers' interests in leather substitutes with comparable qualities. Among various artificial materials designed for leather substitution, polyurethane laminated fabric, namely PU synthetic leather is gaining popularity due to its outstanding abrasion resistance, strength and toughness, chemical and hydrolysis resistance, colorability as well as low temperature flexibility.^{1,2} Despite that this polymer based alternative has been widely introduced in the manufacture of garments, shoes, car seat coverings and other accessories, currently available PU synthetic leather may also present certain inconvenient limitations, the most serious one of which lies in its relatively lower permeability compared with that of genuine leather.³⁻⁵ As already know, ideal clothing or footwear with a high capacity for mass transmission allows the formed perspiration to evaporate promptly when activity level increases; therewith the heat generated by metabolism can be continuously dissipated and regulated such that a constant body temperature is maintained and the so-called human thermal comfort is provided.⁶⁻¹⁰ In contrast to this "breathable" attribute, PU synthetic leather exhibits low permeability, which has inevitably aroused many complaints from customers that the wear comfort is far from comparable to genuine leather. Partly because of this shortcoming, sales of PU synthetic leather began to decline in the latter part of 1984, and there has been no sign of recovery thus far.¹¹

To fulfill the customers' growing requirement for wear comfort, considerable efforts have been devoted by researchers to develop PU leather coating with excellent permeability. For example, C.P.Chwang *et al*¹¹ employed poly (ethylene glycol) 400, ethylene glycol, dimethyl dimethoxysilane, and other strong hydrophilic compound in the preparation of polyurethane resins, which substantially raised the amount of water vapor/oxygen permeating through PU leather coating made with these polymers. In addition, our previous studies^{3-5,12} reported that compared with traditional amorphous counterpart of equivalent thickness, PU leather coating made of thermo-sensitive polyurethane showed more significant enhancement in water vapor transmission rate when the temperature exceeded the phase transition temperature of the segmented polymer. This research made "smart PU leather", i.e. PU leather with warm-keeping at low temperature and high permeability at high temperature, quite possible. Except for such previous studies, few literatures, to the best of our knowledge, have focused on the idea that enhanced permeability of PU leather coating may be achieved by the addition of inorganic fillers, because this thought is contrary to some established principles that adding impermeable filler particles to polymer will lead to a systematic reduction

in mass transport. Physically, such barrier phenomenon can be attributed to the increase in diffusion path length and decrease in effective cross-sectional area available for the transportation of molecules through the composite.^{13,14} Additionally, one of the most frequently used equation to describe the transportation behaviors of filled polymers is the so-called Maxwell model,^{15,16} in which the permeability of a composite composed of a polymer and impermeable fillers can be calculated as follows.

$$P = P_0 \frac{1 - \phi_f}{1 + \frac{\phi_f}{2}} \quad (1)$$

Where, P represents the permeability of the composite, P_0 is the pure polymer permeability and ϕ_f stands for the filler volume fraction, respectively. This model also captures the notion that filler particles obstruct mass transportation and, in spite of its simplicity, is in good agreement with some experimental results in various filled polymer systems.¹⁷ However, the establishment of these conventional principles is based on the assumption that the properties of each phase in a composite are the same as if the other phase were not there, i.e. the surface of the filler particles is completely wetted by surrounding polymer. It does not take the effects of interface between polymer and some special fillers, such as nano particles, into account. Due to its characteristics such as non-toxicity, corrosion resistance, high hardness, UV absorption capacity, antimicrobial activity and low cost, nano-TiO₂ has been widely introduced into many existing materials to design novel products that function unexpectedly.¹⁸⁻²⁰ In this study, a novel *in-situ* organic-inorganic nano-hybrid process was developed to introduce nano-TiO₂ into PU leather coating. In opposition to conventional principles of increased tortuosity and Maxwell model, the modified samples showed both enhanced water vapor permeability (WVP) and gas permeability. To further explain this phenomenon, nitrogen adsorption/desorption measurements were performed to investigate the interfacial structure between polyurethane and nano-TiO₂ particles. More importantly, the *in-situ* organic-inorganic nano-hybrid process developed in this study was carried out simultaneously during the industrialized wet-phase inversion coating-forming method for PU leather manufacture, which promised its possible application on an industrial scale.

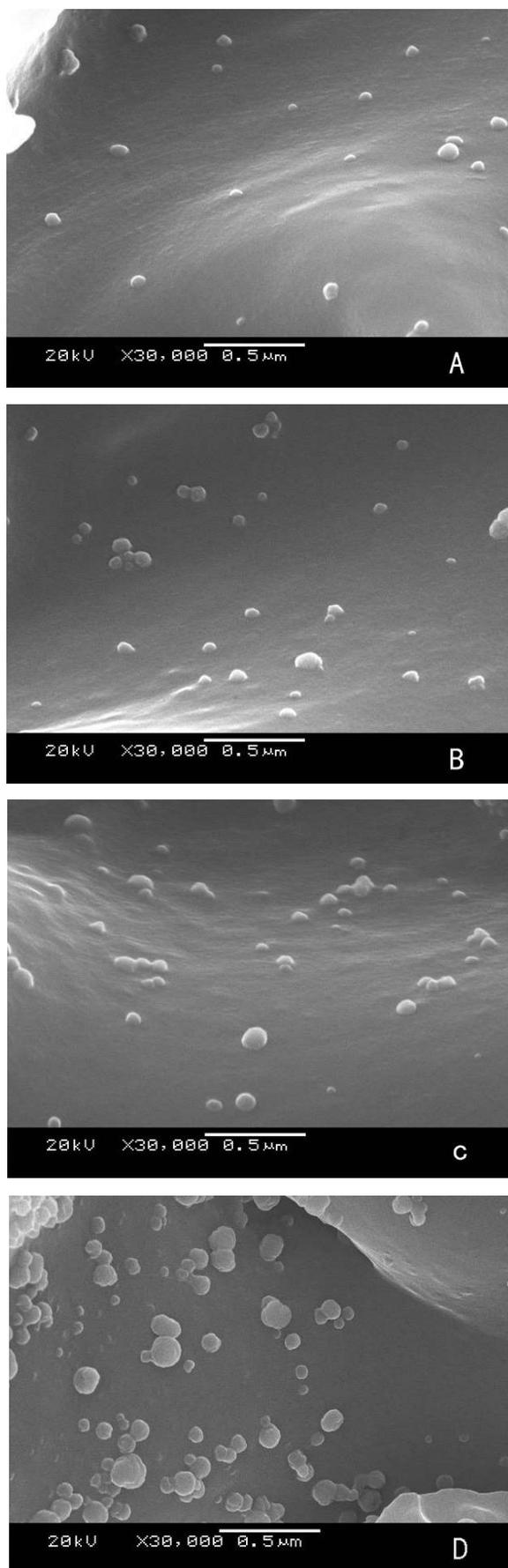


Figure 1: SEM images concerning the cryofractured cross section of PUT membranes: (A)PUT-0.25, (B)PUT-0.50, (C)PUT-0.75, (D)PUT-1.00.

EXPERIMENTAL

Materials

One commercial polyurethane resin (15wt% solution in *N,N*-dimethylformamide) which has been widely used to produce the base of PU synthetic leather via wet-phase inversion coating-forming method, namely 7030 was used in this study. As specified by the manufacturer from Mitsubishi Chemical Industry Co., Ltd. (Japan), it was synthesized from bifunctional diisocyanate (methylene diphenylene diisocyanate, MDI), polyester-based diol (composed of adipate acid, ethylene glycol and *I*, 4-butane diol, with molecular weight of 4000g/mol) and chain extender (ethylene glycol, EG) by two steps of polymerization. In addition, tetrabutyl titanate and acetylacetone which worked as nano precursor and chelating agent respectively were purchased from Aldrich Chemical Co., Inc. (United States). Anhydrous *n*-butanol and acetic acid were obtained from Junsei Chemical Co., Ltd. (Japan). All the chemicals were used as received.

Modification of nano precursor

All the procedures for the modification of nano precursor were performed under dry argon with Schlenk-line techniques to avoid any partial hydrolysis by atmospheric moisture. A predetermined amount of tetrabutyl titanate (converted into TiO₂ concentration of 0.00, 0.25, 0.50, 0.75, 1.00wt% respectively, by weight of the solid content in the PU resin used) was added dropwise under vigorous stirring into an optimized volume of acetylacetone diluted with *n*-butanol (the molar ratio of acac:Ti was 2:1), and then this mixture was ultrasonicated for 1 hour to obtain a transparent and yellow solution.

Preparation of nano-TiO₂ hybrid PU membranes and wet-bases

PU synthetic leather made by wet-phase inversion coating-forming method qualifies for handle, appearance and suppleness similar to genuine leather. In this method, a prewetted woven or non-woven textile is firstly coated with polyurethane dissolved in organic solvent such as *N,N*-dimethylformamide (DMF), and then submerged into a non-solvent (water) bath to coagulate the polymer on the fibrous support. After leaching, squeezing and drying, the wet-base for the manufacture of PU leather is ultimately shaped.²¹ To facilitate the *in-situ* introduction of nano-TiO₂ into the coagulated polyurethane without disturbing the established working procedures mentioned above, a novel *in-situ* organic-inorganic nano-hybrid process, which integrated nano hybridization and industrialized wet-phase inversion coating-forming method, was innovated in this study as follows. In order to disperse nano-TiO₂ particles in the PU membranes and coatings as uniformly as possible, the modified nano precursor prepared above was firstly dissolved in the PU resin under ultrasonic oscillation until a

homogeneous liquid was formed. After deaerated adequately, the mixture was cast on a polytetrafluoroethylene paper and a prewetted non-woven textile respectively using a Gardner knife, which were then immersed in aqueous acetic acid solution at pH 4.5-5.0 for 10 min. During this process, the nano precursor hydrolyzed, and then condensated, *in-situ* producing nano-TiO₂ particles in the PU membranes and coatings. Finally, the hybrid samples (0.2mm for PU membranes, and 0.6mm for the wet-bases with PU coating thickness of 0.2mm) were rinsed in distilled water and the remaining free moisture was further removed by evaporation for 12 hours at 100°C. The hybrid samples (PU membranes and wet-bases) in this study were referred to as PUT-x, wherein PU and T represented polyurethane and nano-TiO₂ respectively, while x showed the TiO₂ concentration in the sample. For example, PUT-0.75 denoted that nano-TiO₂ particles were introduced into the PU membrane or coating with TiO₂ concentration of 0.75wt%.

SEM analysis

Scanning electron microscope (SEM, Cambridge/Leica Stereoscan 440, Leica Cambridge Ltd., Cambridge, UK) was employed to determine the distribution and size scale of nano-TiO₂ in the PUT membranes. All the samples were cryogenically fractured in liquid nitrogen and then coated using aurum sputtering.

Measurement of WVP

WVP of PUT membranes and wet-bases was measured according to ASTM method E 96 Desiccant method, i.e. an open cup containing desiccant was sealed with the specimen in such a manner that the cup mouth defined the area of the specimen exposed to the vapor pressure of the environment. The edges of the specimen were thoroughly sealed to prevent the passage of water vapor into, out of, or around the specimen edges or any portion thereof. Then the assembly was placed in a test chamber at 20°C with a constant relative humidity of 65%. Finally, the weight change of permeation cup with the specimen was recorded after 24 hours and the WVP was calculated by the following equation. The degree of water vapor permeability was expressed as kg/m².d.

$$WVP = \frac{a_1 - a_2}{S} \quad (2)$$

Where, ($a_1 - a_2$): weight change of permeation cup with the specimen (kg), S : area of permeation (m²).

Measurement of gas permeability

Gas (hydrogen, nitrogen and oxygen) permeation testing of PUT membranes and wet-bases was conducted by using Yanaco GTR-10 gas permeability analyzer (Japan). The testing temperature was controlled to be 20°C, and the upstream pressure was kept at 2atm during the experiments. The amount of gas that had permeated through the sample i.e. Q (cm³) as a function of testing time t (s) was

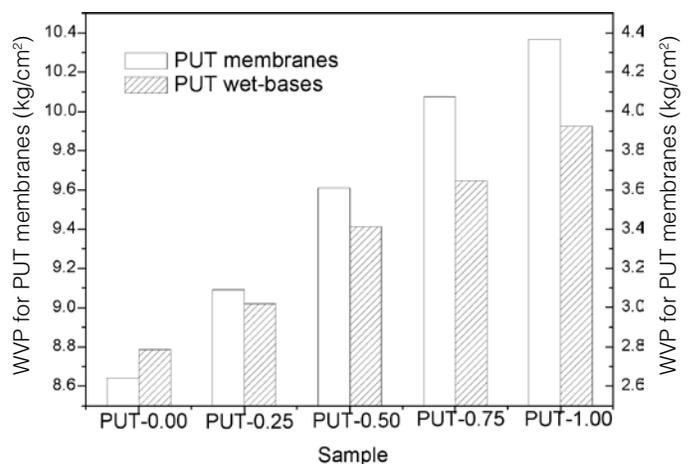


Figure 2: WVP of PUT membranes and wet-bases.

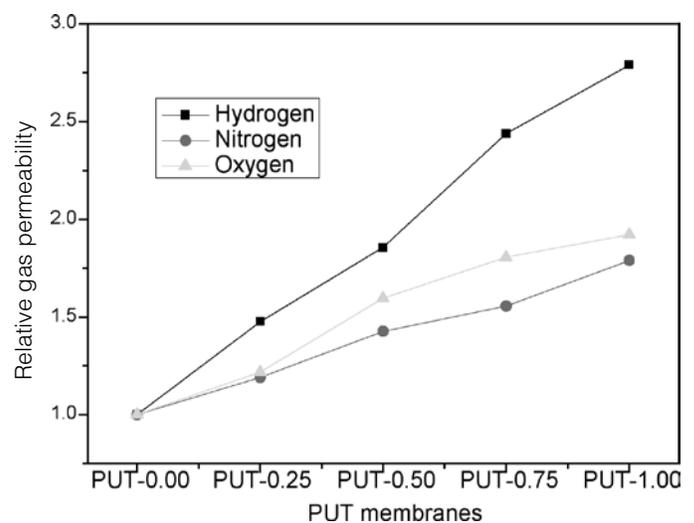


Figure 3: Relative gas permeability of PUT membranes. Relative gas permeability was shown here as the ratio of gas permeability coefficient of the hybrid samples to that of PUT-0.00.

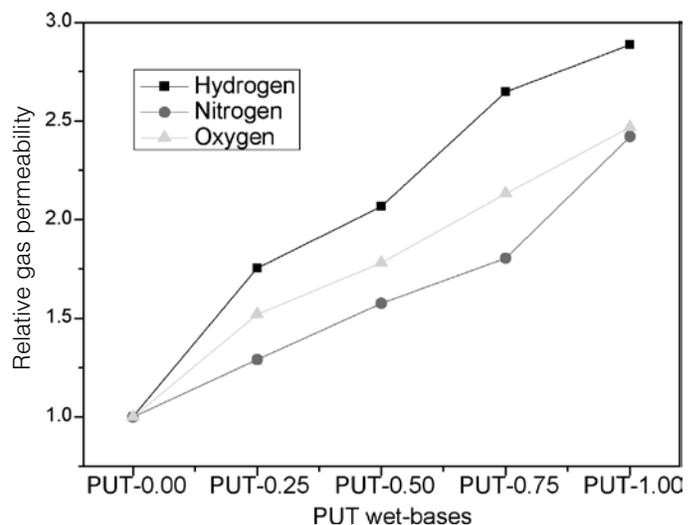


Figure 4: Relative gas permeability of PUT wet-bases. Relative gas permeability was shown here as the ratio of gas permeability coefficient of the hybrid samples to that of PUT-0.00.

automatically presented by the computer connected to the analyzer. Eventually, the plot of Q versus t became linear from which a steady-state gas permeability coefficient P ($\text{cm}^3\cdot\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{atm}$) could be calculated as follows.

$$P = \frac{dQ/dt}{S \times \Delta p / l} \quad (3)$$

Where S and l stand for the permeation area (cm^2) and the sample thickness (cm) respectively; Δp is the pressure driving force (atm).

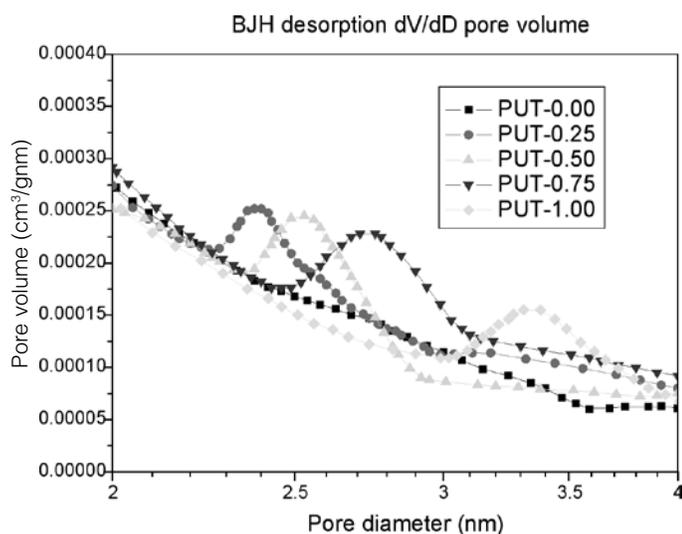


Figure 5: Mesopore size distribution of PUT membranes.

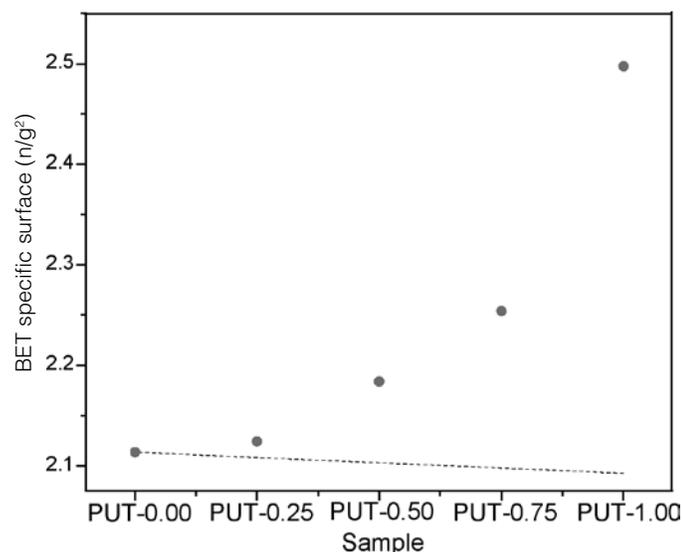


Figure 6: BET specific surface area of PUT membranes. The dashed line represented the theoretical decrease that could be expected when no voids formed between polymer and in-situ-generated nano-TiO₂ particles.

Nitrogen adsorption/desorption experiment

Low-temperature nitrogen adsorption/desorption measurements were conducted to determine the mesopore size distribution and specific surface area of PUT membranes, and experiments were carried out at the boiling temperature of liquid nitrogen (-196°C) by using TriStar 3000 Surface Area and Porosity Analyzer from Micromeritics. Samples were degassed overnight at 100°C under high vacuum prior to analysis. After adsorption/desorption isotherms were obtained in a few hours, classical thermodynamic Barrett–Joyner–Halenda (BJH) theory²² suitable for mesopores with pore width between 2nm and 10nm was employed to determine the mesopore size distribution of all the PUT membranes. To further calculate the specific surface of samples, Brunauer-Emmitt-Teller (BET) theory²² was applied for calculation from the obtained adsorption isotherms. The range of fit for the BET equation was restricted to nitrogen relative pressure (p/p_0) from 0.05 up to 0.35.

RESULTS AND DISCUSSION

Distribution and size scale of nano-TiO₂ particles in PU matrix

Since it has been well established that the distribution and size scale of nano particles in the polymer matrix are quite critical to determine the performance of the nano composites,²³⁻²⁵ how to control the interior morphologies of the prepared PUT coatings is regarded to be an important issue. Basically, there have been at least three methods to prepare nano particle-filled polymer composites thus far, namely melt mixing, solution blending and *in-situ* hybridization. By triggering the hydrolysis and condensation reactions from uniformly dispersed precursor, *in-situ* hybridization is considered as a powerful technique to introduce nano particles into polymer matrix with even distribution.²⁶⁻²⁸ Moreover, via this method, the formation rate of nano particles is dominantly determined by adjustable extrinsic factors such as pH value, temperature and reaction time, which makes the size scale of the *in-situ* generated particles quite manipulated. As for the hybrid PUT membranes containing different TiO₂ concentration prepared in this study, the cross section morphologies of samples were firstly examined by SEM, and the results were given in Figure 1. From these images, a continuous PU matrix with homogeneously dispersed nano-TiO₂ particles could be clearly seen in all cases respectively. Furthermore, the average size of nano-TiO₂ particles was found to be much dependent on the TiO₂ concentration, i.e. with an increasing concentration of TiO₂, the average size of nano particles appeared to increase gradually from 60-80nm in PUT-0.25 to 90-120nm in PUT-1.00 without large agglomerates observed. As already know, tetrabutyl titanate is an active compound, which will induce the formation of undesirable TiO₂ coagulations and even precipitates in organic solvent and resin because of rapid hydrolysis and

condensation.²⁹⁻³¹ In order to achieve ideal size (1-100nm) of TiO₂ particles throughout the PUT samples, acetylacetonate (acacH) was adopted in the present experiment as a chelating agent to reduce the chemical reactivity of the nano precursor. According to prior reports that had already mentioned the reaction between titanium alkoxides and acetylacetonate,^{32,33} the chelating product was assumed to be Ti(OC₄H₉)_{3-x}acac_x based on the following reaction.



By substituting the easily hydrolysable alkoxy groups, the less reactive Ti-acac groups acted as poisons towards hydrolysis and condensation, restraining the presence of TiO₂ coagulations and precipitates in the PU matrix. On the other hand, it was probable that growth of the nano-TiO₂ particles could be inhibited spatially by the PU macromolecular matrix in the present experimental system, which would also stabilize the nano-particles to prevent them from coagulation.

Water vapor and gas permeability of PUT membranes and wet-bases

The water vapor and gas permeability of PUT membranes and wet-bases prepared in this study as a function of TiO₂ concentration were given in Figure 2-4. According to these diagrams, it was worth noting that both the water vapor and gas permeability tended to increase gradually for samples with an increasing concentration of TiO₂. For example, the WVP increased by 5.2%, 11.2%, 16.6% and 20.0% for PUT-0.25, PUT-0.50, PUT-0.75 and PUT-1.00 (membrane samples) respectively compared with that of PUT-0.00, and meanwhile the *in-situ* generated nano-TiO₂ particles also resulted in almost twofold improvement in oxygen permeability for the PU membrane at the highest TiO₂ concentration. Obviously, these results were not consistent with conventional principles of increased tortuosity and Maxwell model. To offer a reasonable explanation, one conjecture was proposed as follows. That was, due to incompatibility between organic polyurethane and inorganic *in-situ* nano-TiO₂, voids occurred at the interface. In addition, the effects of these interfacial voids on the permeability of the polymer could not be ignored and were influential because of the tremendous surface area possessed by nano-TiO₂ and much smaller particle distance. In the process of mass transportation, these voids were beneficial for Knudsen diffusion³⁴ and consequently resulted in an increase in permeability. To confirm this assumption, nitrogen adsorption/desorption measurements were performed to investigate whether these crucial fraction of voids existed in the internal structure of the hybrid PUT samples.

Nitrogen adsorption/desorption

Nitrogen adsorption/desorption measurement provides a convenient way to characterize the pore size distribution and specific surface area of materials containing pores. Based on BJH analysis of the obtained desorption isotherms, a detail of mesopore size distribution of PUT membranes were displayed in Figure 5. On one hand, it was revealed that all hybrid PU membranes contained extra pores after *in-situ* modification, while pure polymer sample exhibited no obvious peaks in the mesopore diameter range. On the other hand, the size of extra pores in hybrid samples increased with an increasing concentration of nano-TiO₂, varying from 2.4nm for PUT-0.25 to 3.3nm for PUT-1.00. Apparently, the exchange of solvent (DMF) and water during wet-phase inversion was a prime cause for void formation in such composite, but it was well known that this mechanism associated voids were macropores with diameter of several micrometers,³⁵⁻³⁸ which could not account for the mesopores detected in this study. Furthermore, no peaks were present in mesopore diameter range for PUT-0.00 that comprised the same solvent component as other hybrid samples. This result could also eliminate the possibility that the extra mesopores in hybrid samples were induced by the exchange of solvent and water. At this point, a conclusion could be drawn that some extra voids, originating from the incompatibility of organic-inorganic phases, did exist in the nano-TiO₂ hybrid PU membranes. Besides, it seemed as if the more nano-TiO₂ *in-situ* introduced, the more significantly such incompatibility worked. This experimental result just supported the conjecture made in the last section, and interpreted the permeability data as presented in Figures 2-4.

Another evidence for the presence of extra voids between PU polymer and nano-TiO₂ particles could be obtained from the analysis of specific surface area of samples. As illustrated in Figure 6, the BET specific surface area of PUT membranes was plotted against the nano-TiO₂ concentration. If *in-situ* generated nano-TiO₂ particles were completely wetted by the organic polyurethane, i.e. no voids were formed at the interface of the two phases; a linear decrease of specific surface with increasing filler concentration was expected (represented by the dashed line). As for the measured specific surface area of filled PU membranes however, sharp departures were recorded compared with the theoretical prediction, i.e. increased TiO₂ concentration was accompanied with higher BET specific surface area of samples. This distinct deviation could also be ascribed to the formation of voids between organic-inorganic phases, which created extra specific surface in the interior of the polyurethane membranes.

CONCLUSIONS

A novel PU/nano-TiO₂ *in-situ* hybrid coating with improved permeability was reported in this study. SEM analysis revealed that homogeneously dispersed nano particles with ideal average size scale could be obtained throughout the PU coatings by the wet-phase inversion *in-situ* hybrid process developed. Due to the formation of voids at the polymer-nano particle interface, which also created extra specific surface area measured in the nitrogen adsorption/desorption experiment, both enhanced water vapor and gas permeability were endowed to the hybrid PU coatings. Since the *in-situ* hybrid process took place synchronously as PU coating coagulated in industrialized wet-phase inversion coating-forming method, the *in-situ* introduction of nano-TiO₂ would not disturb the established working procedures. This novel nanocomposite PU coating with improved permeability may be of great potential for application in PU leather industry, where excellent wear comfort is necessity for the end products.

ACKNOWLEDGEMENTS

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