

# Thermomechanical Analysis of the Biaxially Drawn Ultrahigh Molecular Weight Polyethylene-Reinforced Polyether Polyurethane

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**ABSTRACT:** To understand the thermal fusion and interaction of porous polyurethane composites, the thermomechanical profiles of the heat-compacted composites were described and explained in line with differential scanning calorimetry analysis, FTIR-ATR interpretation, and morphological observations of the oriented ultrahigh molecular weight polyethylene (UHMWPE) under polarized light transmission. The results indicated that the as-cast polyurethane composites are porous and can be consolidated in heat compaction. The consolidated polyurethane composites displayed no thermal contraction in the thermomechanical analysis. Two polyurethane materials, Toyobo TM5 and Tecoflex 80A, were selected for the study. The differences between aromatic and aliphatic polyurethane composites were significant. Aromatic polyurethane composites exhibited characteristic thermal fusion, resulting in a uniform heat-compacted specimen that synergized the thermomechanical advantages of the polyurethane. This thermal fusion led to constraints of UHMWPE and recrystallization of

both UHMWPE and polyurethane. The synergized polyurethane composite demonstrated superior resistance to thermal degradation, observed in both the individual UHMWPE and aromatic polyurethane. Thermomechanical analysis supported the recommendation of using the specific heat compaction at 115°C. This process rendered the aromatic polyurethane composite of highly thermomechanical stability, in agreement with previous findings related to optical transparency and tensile properties. The thermomechanical responses of the composite also provided detailed information about the differences between two samples of similar optical transparency and therefore led to the definition of the synergistic structural composite, a void-free composite with clear evidence. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3088–3095, 2004

**Key words:** biaxially drawn ultrahigh molecular weight polyethylene; polyether polyurethane; composites; thermomechanical analysis; thermal synergizing model

## INTRODUCTION

Mimicking fibrous composite structures of soft tissue is challenged by selecting proper reinforcement materials that do not compromise the preferred elastomeric properties. No man-made fibers are comparable to collagen and elastin of biological origins. Recent publications<sup>1–5</sup> presented a very close approach to make polyurethane composite for soft tissue replacement. Biaxially drawn ultrahigh molecular weight polyethylene (BD-UHMWPE) films, demonstrating an unusually low tensile strength of 50 MPa, were selected as reinforcement materials for polyurethane, the dominant elastomers for soft tissue replacement.

The combination of these two immiscible polymers without using compatibilizers yields some new findings. First, polyurethane composites exhibit excep-

tional optical property.<sup>4</sup> The optical transparency is about 70% under visible light (350–800 nm), very close to that of the polyurethane materials. In addition, a linear relation of the optical transparency ( $T$ ) with the wavelength ( $\lambda$ ),  $T = K\lambda + C$ , was observed regardless of the type of composite evaluated. The  $K$  and  $C$  variables are interpreted as constants closely associated with thermal fusion of the voids and materials interaction between polyethylene and polyurethane. The unusual optical property of the polyurethane composite is apparently  $K$ -dominated, which leads to a linear relation other than the nonlinear response from the individual polyurethane and the  $K$ - and  $C$ -dominated composite. Second, the polyurethane composite has improved mechanical property.<sup>5</sup> The tensile strength of the composite increases up to about 70 MPa, about 20 MPa stronger than that of the BD-UHMWPE (50 MPa). This enhancement was explained under an interpenetrating network of the BD-UHMWPE and the polyurethane. The maximal improvement on tensile properties is attributed to an interlocking system introduced from the recrystallization of both the polyethylene and polyurethane. Finally, polyurethane composites consist of microdo-

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main composites<sup>3</sup> as a result of the infiltration of polyurethane into the porous BD-UHMWPE. These domains are interconnected with microfibril bundles of the drawn UHMWPE and the infiltrated polyurethane.

The exceptional optical and mechanical properties are linked with the thermal fusion of the voids and the formation of interlocking structures in the composite. Although supporting evidences were drawn from morphological observations, optical analyses, mechanical evaluations, and FTIR assays, the study of thermal properties of the polyurethane composites is essential and supportive to the understanding of thermal fusion of voids and materials interaction between the two immiscible polymers. In this study, polyurethane composites were investigated using thermomechanical analysis (TMA), differential scanning calorimetry (DSC), FTIR, and polarized light transmission (PLT). The study focused on the thermal behavior of the polymers and their interaction at specific temperature. FTIR analysis concentrated on the molecular variation as a result of the interaction of two immiscible polymers under heating or a heat-compaction process. The PLT analysis emphasized the changes of the orientation of the drawn UHMWPE.

## EXPERIMENTAL

### Materials

The biaxially drawn ultrahigh molecular weight polyethylene (BD-UHMWPE) film SoluporTM 7P03 was manufactured by DSM Solutech (Heerlen, The Netherlands). It was supplied in a roll of film (porosity ~ 75%; thickness ~ 35  $\mu\text{m}$ ). This BD-UHMWPE film was similar to that reported by Pluyter et al.<sup>6,7</sup> and Gerrits and Lemstra.<sup>8</sup> Briefly, the UHMWPE was dissolved in decalin and extruded into gel films at 180°C. Porous films were formed after evaporation of the solvent at 30°C and simultaneously stretched biaxially (3  $\times$  3). The drawn UHMWPE film had a porous layered structure consisting of microfibril bundles (MB, ~ 400 nm in diameter) and microfibril networks (MN, ~ 80 nm in diameter). The average pore size of the fine pores was about 300 nm (from 0.1 to 100  $\mu\text{m}$ ).

Two polyether polyurethane materials, Toyobo TM5 and Tecoflex 80A, were supplied by Toyobo Co. (Tokyo, Japan) and Thermedics Inc. (Woburn, MA), respectively. The 10% Toyobo TM5/*N,N*-dimethyl formaldehyde (DMF) solution was made by Professor Mitsuo Umezu, Waseda University, whereas the 10% Tecoflex 80A/tetrahydrofuran (THF) solution was produced in Singapore.

### Sample preparation

The composite membranes were made from biaxially drawn UHMWPE films (SoluporTM 7P03) and poly-

ether polyurethane materials (Toyobo TM5 and Tecoflex 80A) following the methods in our previous publications.<sup>2-5</sup> Briefly, the porous biaxially drawn UHMWPE film Solupor TM 7P03 was impregnated in 10% Toyobo TM5/DMF solution and 10% Tecoflex 80A/THF solution for about 3 days and then dried in vacuum to remove the solvent. A translucent composite membrane was therefore obtained. The composite was sandwiched between two Teflon sheets and heat compacted in a laboratory press (LABQUIP Model LP 50; Lab Tech Engineering Co.) under about 18 MPa at temperatures of 95, 105, 115, 125, and 135°C for about 1.5 h. The heat-compaction temperature was recorded by inserting a thermocouple inside the Teflon sheets and reading it with a display (T-Copper Constantan Model 199; Omega). The heat compaction temperature was controlled precisely within a deviation of 1°C. The heat-compacted membrane (HCM) was removed from the Teflon sheets upon cooling to room temperature. The sample membranes were placed in a sealed plastic bag and stored in desiccators for 1 week before specific evaluation.

The polyurethane films were made by solution casting onto a glass plate. The samples were collected after solvent evaporation, kept in sealed plastic bags, and stored in desiccators for 1 week before specific evaluation. Specimens were cut as specified in the individual test conditions.

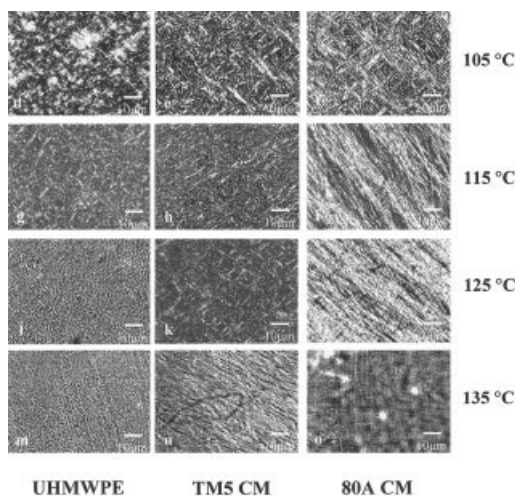
### Thermal analysis

The thermomechanical profiles of the BD-UHMWPE film, polyurethane films, and composite membranes were recorded using a thermomechanical analyzer (TMA 2940; TA Instruments, New Castle, DE). Specimens of 4-mm width of and 15-mm length were mounted onto the film/fiber mode and the machine checked the response of the specimen under a tension of 0.05 N during heating. The thermal behavior of the materials was recorded from 30 to 250°C at a scanning speed of 10°C/min and analyzed using Universal Analysis software (version 2.3C).

The thermal profiles of the BD-UHMWPE film, polyurethane films, and composite membranes were recorded using a differential scanning calorimeter (DSC 2920, Thermal Analyst 3100; TA Instruments). The thermal behavior of the materials was recorded from 40 to 200°C at a scanning speed of 5°C/min.

### ATR-FTIR

ATR-FTIR spectra of the samples were taken in a resolution of 2  $\text{cm}^{-1}$  for 120 scans using a Bio-Rad Excalibur Series (FTS3000; Bio-Rad, Hercules, CA) with an ATR accessory Bio-Rad UMA-500 and a germanium crystal. The peak at about 998  $\text{cm}^{-1}$  was assigned to the stretching of the crystalline ether.<sup>9-11</sup>



**Figure 1** Polarized light transmission photographs of the orientation of UHMWPE in BD-PE films and Toyobo TM5 (TM5 CM) and Tecoflex 80A composite (80A CM) membranes heat compacted at 105 to 135°C.

The  $1175\text{ cm}^{-1}$  peak was attributed to the degradation of polyurethane.<sup>12</sup>

### Polarized light transmission

A polarized light microscope (Optiphot-pol, Nikon, Tokyo, Japan) was used to study the orientation of BD-UHMWPE. The translucent composites were mounted directly on the sample stage while the UHMWPE film was immersed in a refractive index matching oil ( $\sim 1.55$ ; immersion oil for microscopy,  $8\text{ cm}^3$ , ordinary use,  $n_D = 1.516$  at  $23^\circ\text{C}$ , Olympus Optical Co., Tokyo, Japan) before observation. The magnification was calculated using standard grating plates.

The samples of the heat-compact BD-UHMWPE film and the as-cast polyurethane composites were mounted onto the stage during the observation, for the purpose of studying the effect of heat compaction on the orientation of the BD-UHMWPE.

## RESULTS AND DISCUSSION

Figure 1 shows the orientation of the biaxially drawn UHMWPE fibrils under polarized light during series heat compaction. Heat compaction affected the orientation of the UHMWPE fibrils when the compaction temperature was set from 105 to  $135^\circ\text{C}$ . The matrix materials around the UHMWPE fibrils determined the compaction temperature that changed the orientation of the fibrils. Morphological observations showed that the disruption of the orientation of the UHMWPE fibrils occurred at a compaction temperature of  $125^\circ\text{C}$  for the biaxially drawn UHMWPE film,  $135^\circ\text{C}$  for the Toyobo TM5 composite, and  $115^\circ\text{C}$  for the Tecoflex

80A composite. Completely disrupted UHMWPE fibrils were observed at a compaction temperature of  $135^\circ\text{C}$  in Tecoflex 80A composite, resulting in granular extrusion of UHMWPE on the surface of the composite.

The matrix materials for BD-UHMWPE film were the relaxed and nonextended UHMWPE. All the BD-UHMWPE film, heat compacting at a temperature above  $105^\circ\text{C}$ , appeared translucent and homogeneous by visual inspection. The optical transparency of the heat-compact film was approximately up to 40%.<sup>4</sup> It was observed that the optical property changed with the increase of the  $K$  value as reported previously.<sup>4</sup> The increase in  $K$  value was explained as a strong evidence for the thermal fusion of voids by the matrix UHMWPE in heat-compact UHMWPE film. The disruption of the UHMWPE fibrils in BD-UHMWPE film indicated the heat flow of the mobile UHMWPE at a temperature of  $125^\circ\text{C}$ .<sup>13,14</sup> Although the optical transparency of the heat-compact film remained unchanged, the  $C$  value changed dramatically.<sup>4</sup> The change of the  $C$  value was closely associated with the disorientation of the UHMWPE fibrils and fusion of relaxed UHMWPE. The mobile matrix UHMWPE gradually dismantled the oriented UHMWPE fibrils, resulting in nonoriented UHMWPE crystals upon cooling.<sup>15</sup>

The matrix materials for the Toyobo TM5 composite membrane were the infiltrated Toyobo TM5 and the nonextended UHMWPE. This polyurethane composite demonstrated better thermal compaction resistance than that of the BD-UHMWPE film. The UHMWPE fibrils were partially dismantled when the polyurethane composite was heat compacted at  $135^\circ\text{C}$ . On the contrary, the Tecoflex 80A composite showed the worst thermal compaction resistance. The UHMWPE fibrils were partially dismantled when the polyurethane composite was heat compacted at  $115^\circ\text{C}$  and completely disappeared when the polyurethane composite was heat compacted at  $135^\circ\text{C}$ .

The thermal compaction resistance was intimately correlated with the matrix materials that were interacted with the UHMWPE fibrils in the composite. The matrix materials exhibiting a thermal compaction resistance showed a descending order, as follows: Toyobo TM5 > amorphous UHMWPE > Tecoflex 80A. This sequence substantially agreed with the findings of the thermomechanical responses of the pure solution-cast polyurethane membranes, shown in Figures 2 and 3. The Tecoflex 80A was the most mobile phase that was closely interacted with the UHMWPE fibrils. Tecoflex 80A also was the most active polyurethane introducing disruption of the orientation of the UHMWPE fibrils before the drawn UHMWPE fibrils were thermally affected.

The mobility of the matrix materials could be reflected from the thermal response of the UHMWPE

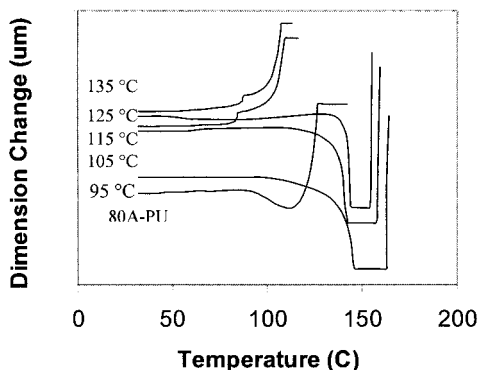


Figure 2 Typical thermomechanical responses of the Tecoflex 80A (80A-PU) and its heat-compacted composites.

fibrils in the candidate materials. Figure 4 shows the DSC curves of the BD-UHMWPE film and its heat-compacted derivatives. The results demonstrated that the oriented UHMWPE fibrils had a melting point at about 142°C (a highly constrained orthorhombic structure of UHMWPE<sup>16-19</sup>). Heat compaction up to 105°C displayed interesting recrystallization of the UHMWPE in the heat-compacted BD-UHMWPE film. The movement of UHMWPE molecules at 95°C under compression drove the UHMWPE into a highly constrained state, in view of the asymmetry of the endothermic peak inclining toward high melting temperature. This momentum seemed to break down when the BD-UHMWPE film was heat compacted at 105°C. The highly mobile UHMWPE eventually incorporated a substantial amount of the orientated UHMWPE and recrystallized it into a less-orientated UHMWPE crystal. This might explain the endothermic peaks (~ 130 and ~ 151°C) in the DSC curve of the BD-UHMWPE film heat compacted at 105°C.

The matrix materials for Toyobo TM5 composite were the amorphous UHMWPE and the Toyobo TM5. It seems the mobile UHMWPE played the same role as

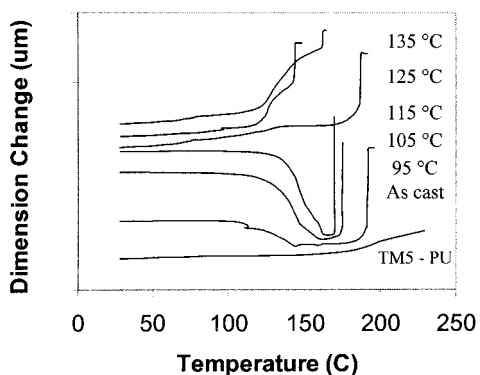


Figure 3 Typical thermomechanical responses of the Toyobo TM5 (TM5-PU)-Toyobo TM5 composite (as-cast) and its heat-compacted composites.

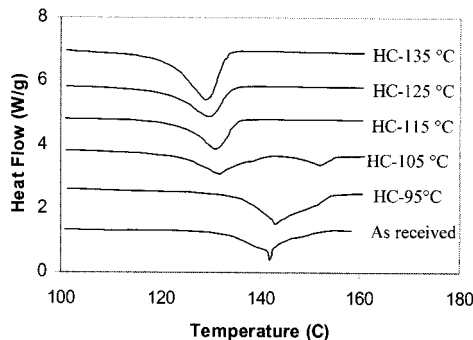


Figure 4 DSC curves of the porous UHMWPE film and its heat-compacted derivatives. Heating speed is at 5°C/min.

that discussed above. However, differences were found in the manner of the aforementioned “break down” and the recrystallization of the captured UHMWPE. Three endothermic peaks (~ 131, ~ 137, and ~ 151°C) were depicted in the break down of the DSC curve (Fig. 5) of the Toyobo TM5 composite heat compacted at 105°C. It might be attributable to the gradient constraint from the heterogeneous matrix materials. The polyurethane matrix might play a higher constraining role to the less-oriented UHMWPE. The recrystallization of the less-oriented UHMWPE in specimens heat compacted above 105°C appears the same regardless of the heat-compaction temperature. It supports the constraint from Toyobo TM5 that successfully encapsulated the oriented and less-oriented UHMWPE.

The matrix materials for Tecoflex 80A composite were the amorphous UHMWPE and the Tecoflex 80A. The DSC curves (Fig. 6) of the heat-compacted Tecoflex 80A composite exhibit a unique phenomenon of high constraint from Tecoflex 80A instead of mobile UHMWPE until the UHMWPE completely disoriented at a compaction temperature of 135°C. The major differences between Tecoflex 80A and Toyobo TM5 composites were that the mobile Tecoflex 80A did not drive the UHMWPE into a highly constrained state

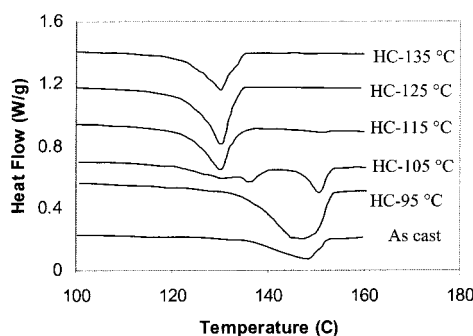
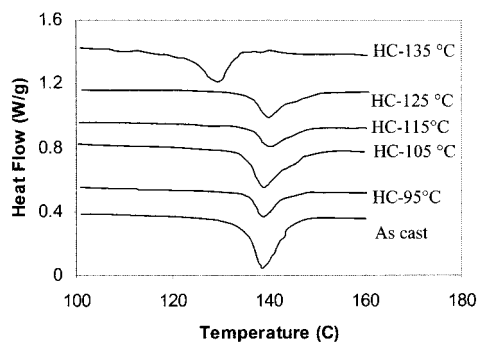


Figure 5 DSC curves of the Toyobo TM5 composite membrane and its heat-compacted derivatives. Heating speed is at 5°C/min.



**Figure 6** DSC curves of the Tecoflex 80A composite membrane and its heat-compacted derivatives. Heating speed is at 5°C/min.

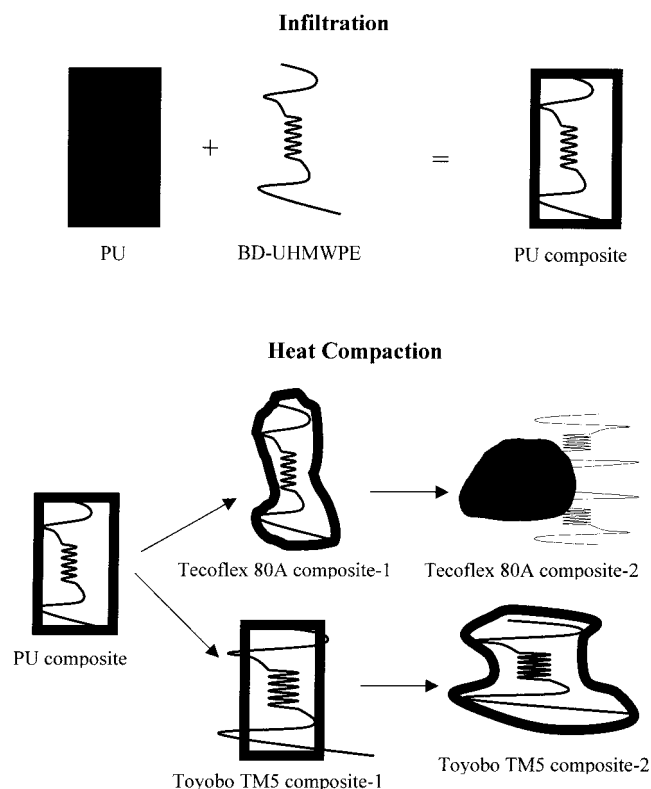
like those occurring in the BD-UHMWPE film and Toyobo TM5 composite. The matrix Tecoflex 80A was much more active than the mobile UHMWPE in constraining the oriented UHMWPE. In the Toyobo TM5 composite, the mobile UHMWPE played the role when the compaction temperature was below 105°C and Toyobo TM5 played the role when the compaction temperature was above 105°C. The oriented UHMWPE held in the cell of Tecoflex 80A was different from that held in the cell of Toyobo TM5 when the samples were both heat compacted at a temperature from 105 to 125°C.

The schematic interaction of the UHMWPE with polyurethane materials during infiltration and heat compaction is depicted in Figure 7, and the illustration shows that a polyurethane like Tecoflex 80A, which is more sensitive to heat compaction, was inclined to wrap the UHMWPE fibrils and insulated them from thermal attack. The UHMWPE could break the insulation only when the expansion was larger than the cohesive force of the mobile polyurethane. The consequence was that the UHMWPE was extruded out of the polyurethane, forming granular UHMWPE. Heat compaction also enhanced the congregation of the UHMWPE fibrils. A polyurethane like Toyobo TM5, which is less sensitive to heat compaction, would let the UHMWPE fibrils expand in the cell that produced the phase 1 composite. This phase 1 composite could be transferred into phase 2 composite when heat compaction allowed the expansion of the matrix polyurethane. Therefore, the matrix material that could introduce thermal fusion of the voids with the reinforcement material was the best candidate material for a composite of optical transparency and probably improved mechanical properties.

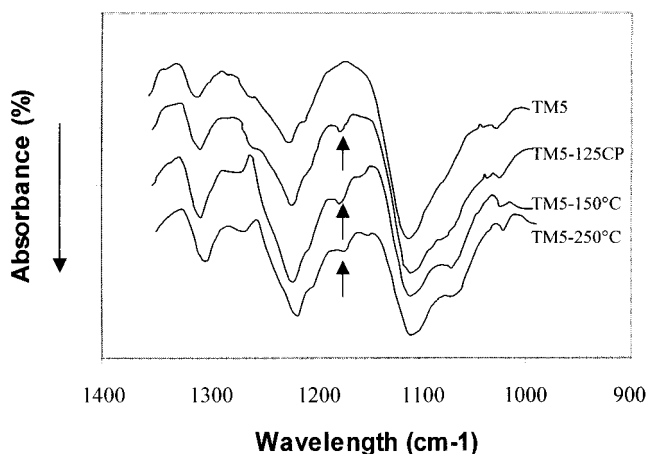
The formation of the synergistic structure in phase 2 Toyobo TM5 composite might improve the tensile properties of the composite. The optimal optical transparency of the Toyobo TM5 composite indicated that the composite had many fewer voids than Tecoflex 80A composite and therefore introduced improved

modulus and tensile strength. Other factors might also affect the mechanical properties of the Toyobo TM5 composite, for example, of recrystallization of the aromatic polyurethane and the partial oxidation of the amorphous UHMWPE.<sup>5</sup> This is because the heat compaction-induced degradation of Toyobo TM5, hypothesized in our previous publication,<sup>5</sup> was based on the lower tensile strength and strain of the treated sample. This degradation was confirmed by FTIR spectra with a characteristic absorption band at about 1175  $\text{cm}^{-1}$  in Toyobo TM5 heat compacted or heating to 250°C (Fig. 8). That Toyobo TM5 composite showed exceptional tensile properties prompted the hypothesis of the stable synergistic structure in phase 2 Toyobo TM5 composite, resulting from the template crystallization onto the BD-UHMWPE.

The synergistic structure in phase 2 Toyobo TM5 composite was supported by data from thermomechanical tests. The BD-UHMWPE film and its heat-compacted derivatives were categorized into three groups<sup>4</sup>: (1) the opaque films (raw and HC 95°C), (2) the translucent films (HC 105, 115, and 125°C), and (3) the highly translucent film (HC 135°C). The optical transparency of the heat-compacted films failed to reveal a difference among the translucent films (HC 105, 115, and 125°C). The thermomechanical tests were designed to provide further evidences for the void fusion of the composites. Figure 9 shows the typical



**Figure 7** Interaction of the UHMWPE with polyurethane during infiltration and heat compaction.



**Figure 8** FTIR-ATR spectra for the effect of heating and heat compaction on the molecules of Toyobo TM5.

thermomechanical responses of the porous BD-UHMWPE film and its heat-compacted derivatives. The results exhibit the differences of thermomechanical responses among the translucent films (HC 105, 115, and 125°C).

The porous UHMWPE film without heat compaction was used as a benchmark for the discussion of void fusion. The UHMWPE film displayed a typical thermal stability to a temperature of about 80°C. The activated UHMWPE might aggregate together and produce a significant shrinkage of the film. The thermomechanical response was recorded and a significant decrease of the dimension appeared from about 115 to 140°C. The shrinkage was designated as thermal contraction ( $T_c$ ). The contraction of the specimen ceased and then registered a period of zero-dimension change [i.e., moiety tautening ( $T_{mt}$ )] to a temperature of about 160°C. The following sudden increase in dimension [i.e., moiety breaking ( $T_b$ )] indicated the complete melting breakdown of the polymers.

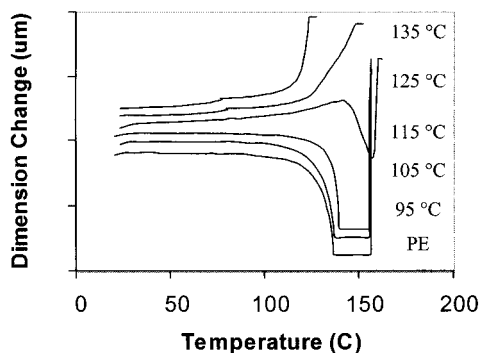
The porous UHMWPE film heat compacted at 105°C demonstrated higher optical transparency than that of the film heat compacted at 95°C. The difference in thermomechanical responses between these two samples was in the range of  $T_{mt2}$  to  $T_{mt1}$ . The  $T_{mt1}$  of the film heat compacted at 105°C was higher than that of the film heat compacted at 95°C. In the sample heat compacted at 115°C, the value of the  $T_{mt2} - T_{mt1}$  was zero. This sample was very different from any other film heat compacted at or below 105°C, showing a period of increase in dimensions [i.e., thermal expansion ( $T_e$ )], and following a decrease or shrinkage in dimension and sudden breakage.

The porous UHMWPE films heat compacted at 125 and 135°C, although optically different, were thermomechanically similar. Both films recorded only a thermal expansion, except the film heat com-

packed at 125°C was more ductile than the film heat compacted at 135°C. The ductility of the film heat compacted at 125°C might be attributable to less recrystallization of the UHMWPE, as indicated in Figure 4.

The thermal contraction ( $T_c$ ) was an indication of voids in the specific samples and the moiety tautening ( $T_{mt}$ ) was a marker for the balance between aggregation of the relaxed UHMWPE and orientation of the extended UHMWPE. The zero ( $T_{mt2} - T_{mt1}$ ) was a parameter to show that the heat-compacted sample was void free. Correlation of this void-free composite was the difference of the  $K$  values recorded from the samples heat compacted below and above 105°C.<sup>4</sup> The higher value of  $K$  indicated the lower volume of voids. Correlation of the interaction of the matrix materials with the fibril material (showing no moiety tautening but thermal expansion) was the change of the  $C$  value.<sup>4</sup> The decrease of the  $C$  value indicated that the oriented UHMWPE was highly constrained and about to collapse. The sudden increase of the  $C$  value demonstrated that the constraints on the UHMWPE were removed, resulting in a more homogeneous UHMWPE phase and higher optical transparency.<sup>4</sup> Therefore, the characteristic three groups of the heat-compacted UHMWPE films were controlled by both the  $K$  and the  $C$  values. From opaque films (raw and HC 95°C) to the translucent films (HC 105, 115, and 125°C) it was  $K$ -dominant, whereas from the translucent films (HC 105, 115, and 125°C) to the highly translucent film (HC 135°C) it was  $C$ -dominant; in other words, it was the effects of removal of voids ( $K$ -dominant) and increase of the interaction between the matrix and reinforcement materials ( $C$ -dominant).

Tecoflex 80A composites could be categorized into two groups in view of the optical transparency<sup>4</sup>: the translucent films (raw and 105°C) and the highly translucent films (HC 95, 115, 125, and 135°C). The thermomechanical responses of



**Figure 9** Typical thermomechanical responses of the porous BD-UHMWPE (PE) and its heat-compacted films.

Tecoflex 80A composites (Fig. 2) did not show a logical sequence of heat compaction. However, the void-free composites might be the samples heat compacted at 115 and 135°C. The samples heat compacted at 95, 105, and 125°C recorded a significant thermal contraction and a completely different value of  $(T_{mt2} - T_{mt1})$ , where both  $T_{mt2}$  and  $T_{mt1}$  were different from each other. This irregularity might be attributable to the irregularity of the heat-compacted samples that were treated above 95°C. As mentioned in our previous study,<sup>5</sup> making a sample of Tecoflex 80A composite heat compacted above 95°C was always difficult because of the uncontrollable shrinkage of the samples after heat compaction, which might be the result of the reorientation of the UHMWPE fibrils indicated in Figure 1.

The optical transparency<sup>4</sup> of the Toyobo TM5 composites was recorded in such a clear way of an ascending sequence to HC 115°C and of a descending sequence to HC 135°C, as follows: raw < HC 95°C < HC 105°C < HC 115°C > HC 125°C > HC 135°C.

The thermomechanical response of the Toyobo TM5 composites (Fig. 3) shows that the samples heat compacted at 115, 125, and 135°C are void free and the most ductile sample leads to the highest optical transparency. The samples heat compacted at 95 and 105°C followed the rule of the least value of  $(T_{mt2} - T_{mt1})$ , which marks a sample in which the fewest voids exist. The near zero range of  $(T_{mt2} - T_{mt1})$  indicated that the matrix materials were different polymers. It was an exemplary case of the heat-compacted polyurethane composites when the optical transparency was optimized at the critical point (maximal  $K$  and  $C$  values) of heat-compaction temperature. At this temperature (HC 115°C) the heat compaction did not introduce significant changes to the integrity of the UHMWPE fibrils. An increase of the  $K$  value might be an indicator that the mobile matrix UHMWPE filled the voids, whereas a decrease of the  $K$  value might experience a repulsion of the polyurethane cells that encapsulated the oriented UHMWPE and the matrix UHMWPE. Although heat compacting above 115°C did not introduce improved optical properties, it did not mean the composite could accommodate thermal contraction and moiety taunting. The thermal expansion related to an increase of the  $C$  value might be suitable only for self-reinforced polymer composite.

The thermomechanical responses of the composites provided detailed information about the thermal fusion of the voids and the explanations filled the blanks left by the description of the optical transparency in our previous report.<sup>4</sup> Most important, the thermomechanical responses defined the phase 2 Toyobo TM5 composite as the void-free composite that could be achieved through heat compaction at a temperature above 115°C. The best composite is of high tensile

strength and high optical transparency as well. The synergistic structural Toyobo TM5 composite is also a void-free composite.

## CONCLUSIONS

BD-UHMWPE-reinforced polyether polyurethane composites made from solution casting and heat compaction demonstrated characteristic optical transparency and improved mechanical properties, especially those made from the aromatic polyurethane Toyobo TM5. The results based on thermomechanical analysis with the support of DSC profiles, FTIR-ATR analysis, and morphological observations under polarized light transmission reveal that the aromatic PU can be cast onto the porous BD-UHMWPE and successfully heat compacted to reduce the internal voids in the composite. This is attributed to the recrystallization of Toyobo TM5 in the composite that can be extended synergistically with the crystalline UHMWPE. The synergy between the PU and UHMWPE provides heat resistance of the oriented UHMWPE and degradation resistance of the PU. It also supports the hypothesis of an interlocking system previously made for improving mechanical properties and the  $K$ -dominant factor for linear relation of optical transparency with the incident wavelength. The thermomechanical responses of the composite materials also yield more details that are important but not obtained from the explanation of the optical transparency. Most important, the thermomechanical responses define the synergistic structural composite as a void-free composite with substantial evidences. The investigations provide practical guidance for materials selection and process optimization in making BD-UHMWPE/PU composites.

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