JOURNAL OF MATERIALS SCIENCE **39** (2004) 5673– 5682

Sensors for chemicals based on electrically conductive immiscible HIPS/TPU blends containing carbon black

E. SEGAL[‡], R. TCHOUDAKOV[‡], M. NARKIS[‡,*], A. SIEGMANN[§]
[‡]Department of Chemical Engineering and [§]Department of Materials Engineering,
Technion—Israel Institute of Technology, Haifa 32000, Israel
E-mail: narkis@tx.technion.ac.il

Carbon Black (CB)-containing immiscible polymer blends based on high-impact polystyrene/thermoplastic polyurethane (HIPS/TPU) were studied as sensing materials for an homologous series of alcohols, including, methanol, ethanol and 1-propanol. The studied immiscible blend was designed to exhibit a double-continuity structure i.e., the CB particles form chain-like network structures within the TPU phase, which forms a continuous phase within the HIPS matrix. Extruded HIPS/TPU/CB filaments produced by a capillary rheometer process at various shear rate levels were used for the sensing experiments. All filaments displayed a selective resistance changes upon exposure to the various alcohols combined with reproducibility and recovery behaviour. An attempt is made to identify the dominant mechanisms controlling the sensing process in a CB-containing immiscible polymer blend characterized by a double-continuity structure. The distinct structure and composition of the HIPS/TPU interphase region were found to have a crucial role in the sensing mechanism, determining the selectivity of the filaments toward the studied alcohols. Additionally, the sensing performance of HIPS/TPU/CB system is compared to recent results for TPU/CB compounds, polypropylene/TPU/CB and HIPS/ethylene vinyl acetate/CB immiscible polymer blends.

1. Introduction

In recent years, few studies on sensing materials based on conductive carbon black (CB)-containing polymer blends have been reported. Miscible poly(vinyl acetate) and poly(methyl methacrylate) blends have been used to produce electrically conducting CB-containing compounds of sensitive resistance to the nature and the concentration of an analyte in the vapor phase [1]. Furthermore, these miscible blends exhibited enhanced analyte discrimination compared to reference CB-containing single polymers. Miscible binary polymer blends offer the opportunity to develop a diversity of polymer compounds detector arrays. Narkis *et al.* [2, 3] have introduced a new concept of liquid sensing materials based on electrically conductive CB-containing immiscible polymer blends. The multiphase nature of these systems provides an opportunity for the CB particles to distribute nonuniformly within the phases, due to the different properties of the blend components [4–6]. Thus, unique structures may be formed, determining the material properties and performance. Immiscible polymer blends of polypropylene(PP)/nylon6(Ny6)/CB and high impact polystyrene(HIPS)/ethylene vinyl acetate copolymer(EVA)/CB were used to produce electrically conductive filaments by a capillary rheometer process. These blends were designed to have a double-percolation structure associated with a low CB content. Liquid contact/drying cycling of the filaments exhibits high sensitivity combined with reversible sensing resistance changes. Thus, the feasibility of the concept of conductive immiscible polymer blends as sensor materials has been demonstrated; however, the mechanisms involved were not elucidated.

Recently, an attempt was made to identify the dominant mechanisms controlling the sensing process in a CB-containing immiscible polymer blend characterized by a co-continuous structure [7]. The mechanisms governing the resistance increase upon exposure of the studied systems to several analytes are more complex compared with that of a single polymer system with CB. It was suggested that in immiscible polymer blends the interphase region and its continuity play a significant role in the liquid transport process. In this study, the electrical resistivity of CB-containing polypropylene/thermoplastic polyurethane (PP/TPU) filaments was selectively sensitive to a homologous series of

---

[*]Author to whom all correspondence should be addressed.

alcohols. The polar liquids preferentially permeate through the weak PP/TPU interfaces, followed by selective sorption by the TPU phase. Consequently, swelling of the TPU phase results in the modification of the dispersed TPU particle size and shape which in turn affects the structure of the system in two hierarchies i.e., the continuity of the dispersed phase within the PP matrix and/or the continuity of the CB network. Furthermore, it was suggested that the outstanding resistance reproducibility and recovery behaviour of the PP/TPU/CB sensor may be attributed to the restricted swelling ability of the TPU particles imbedded in the intact, stable PP matrix. It has been suggested that the nature of the blend components, blend composition, CB content, filament's extrusion temperature and production shear rate level are all significant parameters in determining the filament's structure and the resultant sensing properties. Thus, from a practical point of view, utilizing an immiscible multicomponent matrix, rather than a single polymer, offers the possibility to widely tailor suitable sensor systems for a variety of desired applications.

The present paper addresses the structure, electrical conductivity and liquid-sensing properties of CB-containing immiscible multiphase matrices consisting of HIPS as the major phase and TPU as the minor dispersed phase. A series of electrically conductive filaments were produced by a capillary rheometer process. The electrical resistance of these filaments was found to be selectively sensitive to various alcohols. The structure/electrical resistivity/sensing relationships were studied in regard to the reference single polymer/CB compounds i.e., TPU/CB [8] and HIPS/CB. Furthermore, the effects of matrix and dispersed phase polymers nature were studied in regard to the results recently reported for PP/TPU/CB [7] and HIPS/EVA/CB blends [3].

2. Experimental

2.1. Materials

The polymers used in this study were HIPS and a polyether-type thermoplastic polyurethane (TPU). The properties of the component polymer are given in Table I. The conductive CB used was Ketjenblack EC-600 (Akzo-Nobel, Netherlands).

2.2. Blends preparation

All blend ratios described in the text relate to weight ratios. The CB content within the blend is referred to in the text in phr (parts per hundred, by weight). Blends were prepared by a standard procedure of melt mixing of a dry-blended CB and the polymer components in a Brabender Plastograph equipped with a 50 cm^3 cell. The components were compounded at 190°C for approximately 15 min. The resulting blends were then compression moulded at 190°C.

2.3. Rheological studies

Rheological studies were conducted using an Instron capillary rheometer mounted on an Instron TT-D machine. Samples prepared by melt-mixing in the Brabender Plastograph were extruded into filaments using the capillary rheometer at various temperatures of 190, 210 or 230°C. A capillary 5 cm (2 in.) in length and 0.127 cm (0.05 in.) in diameter ($L/D = 40$) was used. The blends were extruded at various crosshead speeds, ranging from 0.05 to 50 cm/min, providing an approximate shear rate range of 3–3000 s^{-1}. The filaments were collected (without any drawing after extrusion) and used for electrical conductivity measurements, sensor analysis and microscopy observations.

2.4. Resistivity measurements

The electrical resistivity measuring method of the samples prepared depended on the geometry produced by a specific processing method and on the resistivity level of the sample.

The volume resistivity of compression-moulded samples was measured (DIN-53596) using a Keithley Electrometer 6514 instrument and a 240A high-voltage supply from Keithley Instruments. For samples with high levels of conductivity, a Sorenson power supply, model QRD 60-1,5, was used. Silver paint was applied to minimize contact resistance between the sample and the electrodes. A filament resistivity was measured as follows: Silver paint was applied to mark several locations on the surface of the filament to ensure contact between the sample and the electrodes. The resistance between two silver marks along the specimen was measured using a Keithley Electrometer 6514 instrument, and volume resistivity was calculated. Resistance was measured at several locations of each filament and averaged to ensure reliable results.

2.5. Sensor analysis

For sensor analysis, 5 mm long filaments were used. A small amount of silver paint was applied at the filaments' ends where electric wires were connected (the

TABLE I Properties of component polymers used

Polymer	Grade	Source	MFI (g/10 min)	T_g[a] (°C)
High-impact polystyrene (HIPS)	Galirene HT-88-5	Carmel Olefins (Israel)	5	98.5
Thermoplastic polyurethane (TPU)	Estane 58866	BF Goodrich (USA)		−45
Polypropylene (PP)	Capilene R-50	Carmel Olefins (Israel)	12	−1.3
Ethylene vinyl acetate (EVA) (vinyl acetate content = 9%)	Escorene UL-209	Exxon (USA)	2	

[a] determined by DMTA.

silver paint's resistivity was insensitive to the studied solvents). Liquid sensing experiments were performed by immersion/drying cycles along with continuous monitoring of the changing resistance. Detailed description of the electrical measurement apparatus has been described in detail elsewhere [7, 8].

All data are presented as relative resistance, i.e., R_t/R_0, where R_0 is the initial resistance of the sensor and R_t is the measured resistance at time t.

The following liquid solvents were used: methanol, ethanol, 1-propanol. All measurements were preformed at ~25°C.

2.6. Morphological characterization

Scanning Electron Microscopy (SEM) of freeze-fractured surfaces was performed using a Jeol-JSM 5400, at an accelerating voltage of 15 kV. Samples were gold sputtered prior to observation.

2.7. Thermal analysis

Dynamic mechanical thermal analysis (DMTA—Perkin Elmer Series 7) was performed in the three points bending mode at 1 Hz. Heating was carried out under nitrogen atmosphere, at a rate of 3°C/min.

2.8. Sorption experiments

Sorption of alcohols was studied using an immersion/weight gain method at a constant temperature of 25°C. Compression moulded samples, 1.2 mm thick, were immersed in glass bottles containing the respective solvents. At various time intervals, the specimens were removed from the solvent, wiped off by filter paper and weighed. Solvent content in the samples at time t was calculated as:

$$\%\text{Sorption} = (\text{Weight at time } t - \text{Initial weight}) \times 100/\text{Initial weight}$$

2.9. Dissolution experiments

Compression moulded samples were immersed in glass bottles containing the respective solvents. At various time intervals, the specimens were removed from the solvent, dried in a vacuum oven at room temperature for 24 h and weighed. Weight loss of the samples at time t was calculated as:

$$\%\text{Weight loss} = (\text{Initial weight} - \text{Weight at time } t) \times 100/\text{Initial weight}$$

3. Results and discussion

3.1. Extruded filaments

3.1.1. Resistivity-shear rate relationships

CB-containing extruded filaments were produced by a capillary rheometer process at various shear rates, and their resistivity values were measured. Fig. 1 depicts the effect of extrusion shear rate level on the resistivity of the HIPS/TPU(65/35) + 2 phr CB blend extruded at various temperatures. At this composition, the TPU phase forms a co-continuous structure within the HIPS matrix and the CB particles form a conductive network within the continuous TPU phase. The exact structure of this blend will be discussed in detail later on. Filaments extruded at 210°C exhibit relatively constant electrical conductivity values throughout the intermediate and high shear rate range. At low shear rates an uncommon slight resistivity decrease (of less than one order of magnitude) with extrusion shear rate is observed. The 190°C extruded filaments exhibit a similar behaviour at the lower shear rate level however, this slight resistivity decrease is followed by a moderate resistivity increase toward the initial resistivity values at the higher shear rates. These relatively constant resistivity values indicate the formation of a stable, well-established conductive structure resulting from a combination of a significantly high effective CB content within the dispersed TPU phase and the continuous structure of this phase within the HIPS matrix, observed

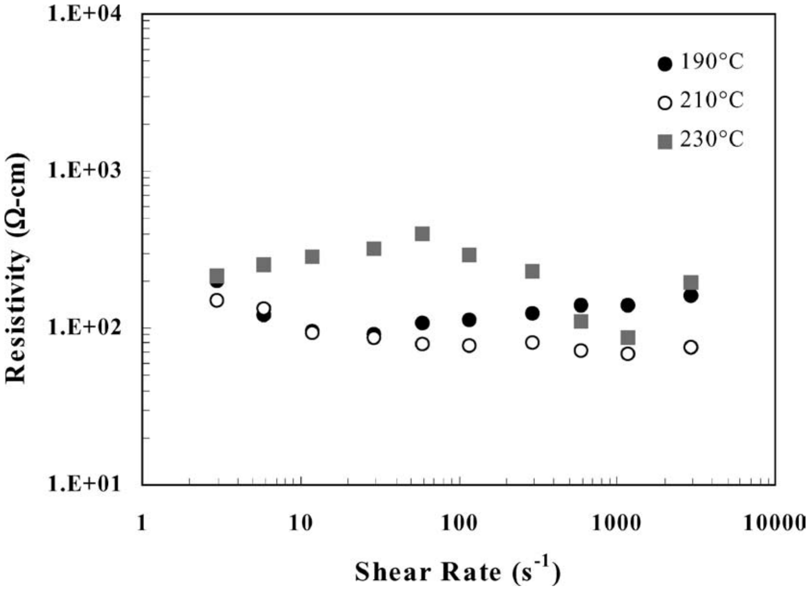

Figure 1 Resistivity vs. extrusion shear rate of HIPS/TPU(65/35) +2 phr CB filaments extruded at various temperatures.

by SEM for all shear rates studied (not shown here). The blend extruded at 230°C exhibits first a slight resistivity increase followed by a moderate decrease as the shear rate increases. This complex behaviour may be attributed to the inclination of CB networks to undergo simultaneous opposing processes of rupture and reagglomeration under shear flow.

3.1.2. Sensing properties of extruded filaments

Fig. 2 depicts the relative resistance, R_t/R_0, of HIPS/TPU(65/35) + 2 phr CB filaments (extruded at 210°C) produced at various shear rates, as a function of exposure time to an homologous series of alcohols (methanol, ethanol and 1-propanol). Initial resistance values of the filaments were: $6.5 \times 10^3\ \Omega$ (produced at low shear rate), $4 \times 10^3\ \Omega$ (intermediate shear rate) and $3 \times 10^3\ \Omega$ (high shear rate). In a single cycle, filaments were immersed for 4 min in a given alcohol and then allowed to dry in air for 9 min. Five sequential cycles were performed for each specimen. Each data point in Fig. 2 represents an average of three studied different filaments (the experimental error was always lower than 5%). All filaments displayed an increasing resistance upon exposure to the various alcohols and a tendency to return to their initial resistance values during the drying step.

The highest resistance increase, namely, the highest sensitivity, is observed for filaments exposed to 1-propanol (see Fig. 2c), whereas the reference TPU/CB system showed an opposite tendency, namely,

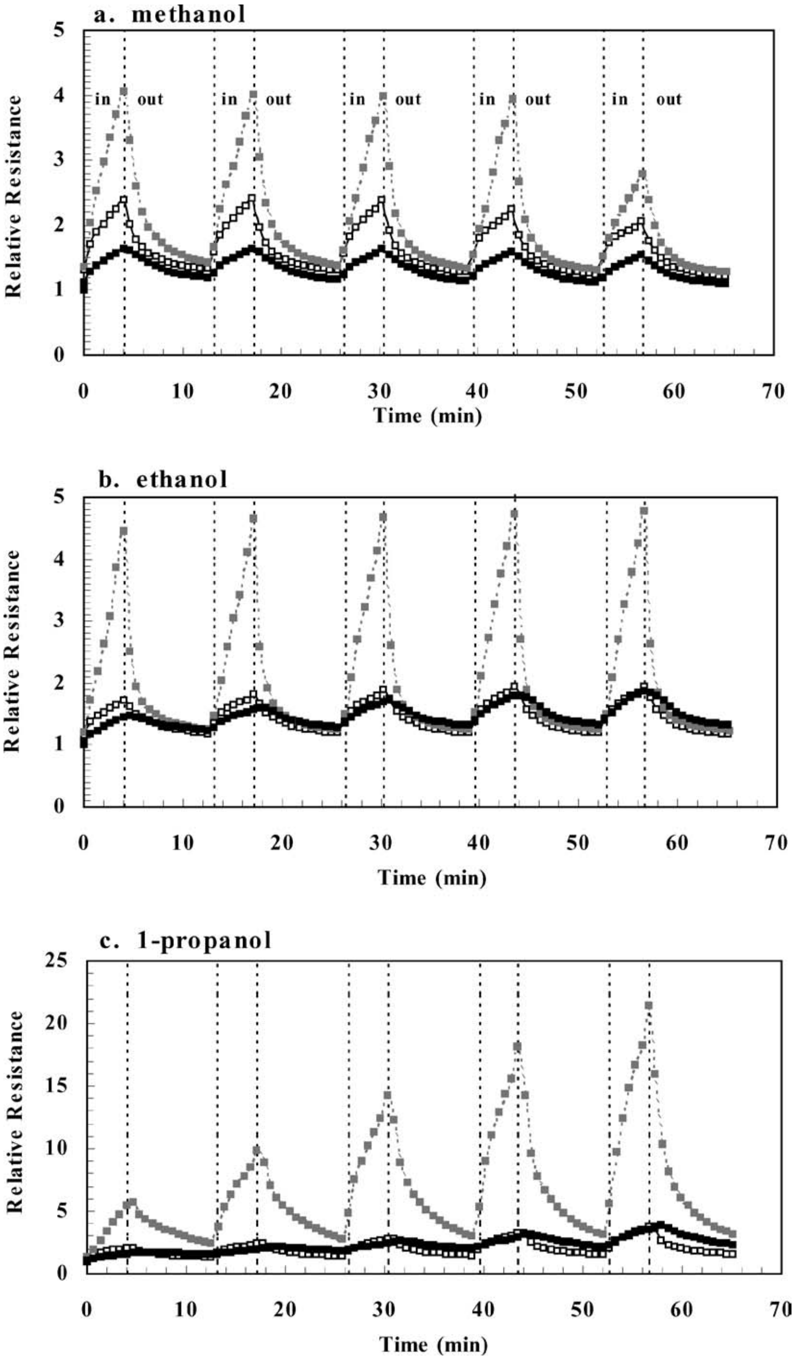

Figure 2 Relative resistance vs. exposure time to methanol, ethanol and 1-propanol, of HIPS/TPU(65/35) + 2 phr CB filaments, produced at different shear rates: (□—6 s^{-1}, (▨)—60 s^{-1} and (■)—600 s^{-1} (extrusion temperature 210°C).

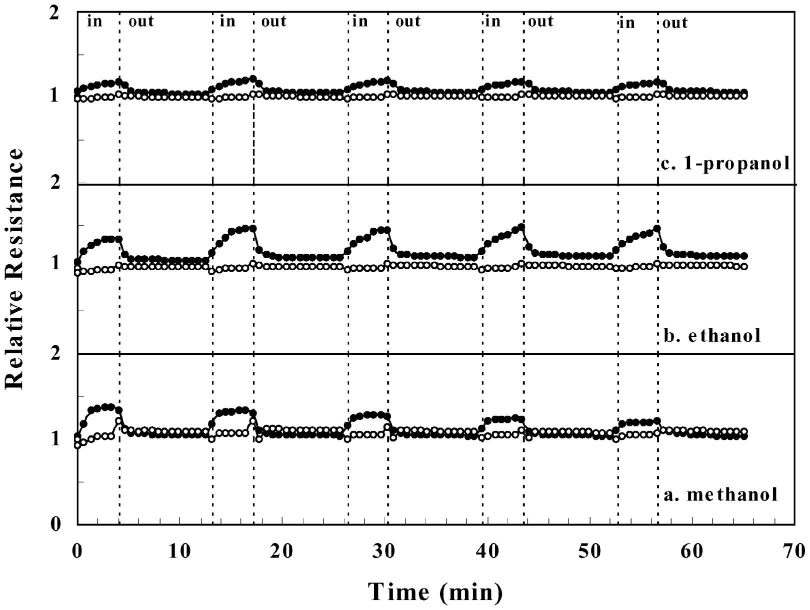

Figure 3 Relative resistance vs. exposure time to methanol, ethanol and 1-propanol, of HIPS/4 phr CB filaments, produced at different shear rates: (●)—6 s^{-1}, (○)—60 s^{-1} (extrusion temperature 210°C).

the highest sensitivity toward methanol [8]. HIPS/CB filaments were also exposed to the same homologous series of alcohols and studied as a second reference system. Fig. 3 depicts the relative resistance, R_t/R_0, of HIPS/4 phr CB filaments (extruded at 210°C) produced at various shear rates, as a function of exposure time to methanol, ethanol and 1-propanol. Initial resistance values of the filaments were: 5.5×10^3 Ω (produced at low shear rate) and 6×10^4 Ω (intermediate shear rate). Filaments produced at low shear rate levels are most sensitive to ethanol, while filaments produced at intermediate and high shear rates are not sensitive to the studied alcohols, exhibiting negligible resistance changes upon exposure. Furthermore, the sensitivity displayed by these filaments is significantly lower than that observed for the HIPS/TPU/CB filaments (see Fig. 2). Similar results were observed by Li *et al.* [9] who studied the electrical response of PS/CB composites prepared by polymerizing styrene monomer in the presence of CB. They have reported that the responsivity of these composites upon exposure to highly polar solvents, such as methanol and ethanol, is extremely low. Thus, the different selectivities and sensitivities exhibited by the reference TPU/CB and HIPS/CB systems compared with those exhibited by the HIPS/TPU/CB system, suggest that the sensing mechanism of the immiscible blend is different from that of the reference individual components with CB.

The morphology, electrical properties and thermal behaviour of CB-containing HIPS/TPU blends (compression moulded) were investigated to help understand how the structure of these blends correlates with the observed sensing properties.

3.2. Compression moulded samples

3.2.1. Morphology-resistivity relationship

The neat HIPS/TPU blend morphology studied at a 65/35 blend ratio is depicted in Fig. 4a, showing irregular structures of TPU dispersed within the HIPS matrix,

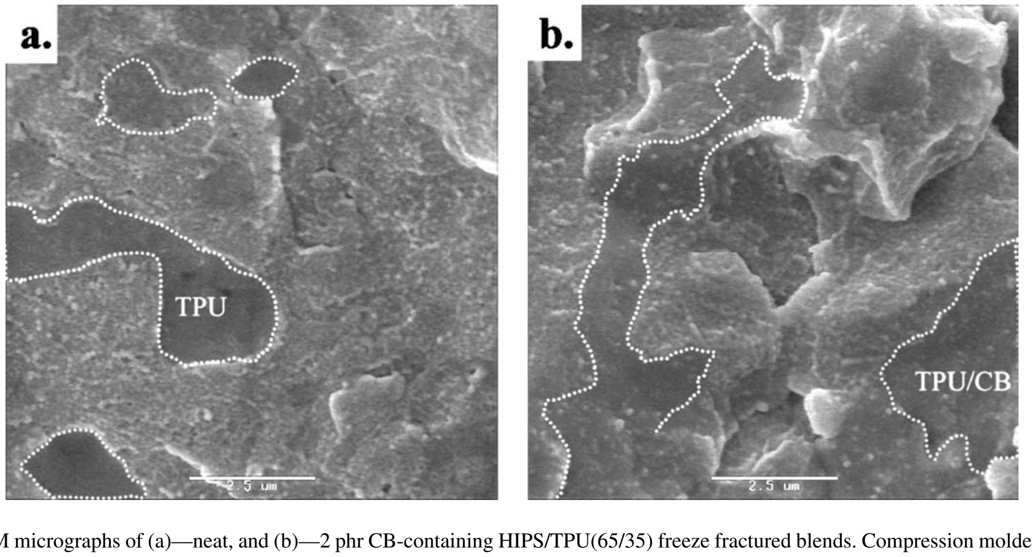

Figure 4 SEM micrographs of (a)—neat, and (b)—2 phr CB-containing HIPS/TPU(65/35) freeze fractured blends. Compression molded specimens.

seemingly approaching the onset of a co-continuous structure. The adhesion between the TPU particles and the HIPS matrix seems rather good, as no gaps between the two polymers are observed. This strong adhesion is further manifested by the freeze fracture propagating through both phases rather than along the interface between the two polymers (see Fig. 4a).

The morphological features of the 2 phr CB-containing HIPS/TPU(65/35) blend are presented in Fig. 4b. The CB particles are preferentially located within the TPU phase, as also indicated by the resistivity measurements discussed below. This is due to the fact that polymers of higher surface tension tend to better interact with the dispersed CB particles (having relatively high surface tension values) [5, 6]. On addition of CB, the blend maintains its co-continuous structure as in the neat case, with no apparent reduction in the dispersed phase dimensions. The two phases appear to adhere well to each other, making it difficult to distinguish between them. This indicates that the incorporation of CB may enhance the interaction between the polymers, which could be the result of an intrinsic interfacial activity of CB particles responsible for a decrease in the HIPS/TPU interfacial tension [7, 10]. However, it should be emphasized that the observed effect of CB on the HIPS/TPU system is rather weak compared with previously studied immiscible polymer blends such as PP/TPU [7] and HIPS/EVA [6].

The percolation threshold of the HIPS/TPU(65/35) blend is achieved below 2 phr CB (the volume resistivity of the 2 phr blend is 4.75×10^3 Ω-cm)—lower than the individually filled HIPS or TPU (found to percolate at 2 and 3 phr CB, respectively). The higher percolation threshold of the TPU/CB system in comparison to HIPS/CB system, implies the tendency of CB to locate preferentially in the TPU phase within the HIPS/TPU blend. Thus, the enhancement of conductivity in the HIPS/TPU blend is achieved via double percolation, structural and electrical. The CB particles form chain-like structures within the TPU phase, which exhibits phase continuity within the HIPS matrix.

3.2.2. Thermal behaviour

The dynamic mechanical properties of the HIPS/TPU(65/35) and the HIPS/TPU(65/35) + 2 phr CB blends, in comparison to those of the neat HIPS and TPU (after Brabender processing and compression moulding at 190°C), as depicted in Fig. 5, are of great interest. Energy dissipation under mechanical cycling as a function of temperature is expressed as the loss modulus. The neat TPU (containing "hard" and "soft" segments) exhibits a peak at −45°C, attributed to the T_g of the "soft" phase. The T_g of the "hard" domains is not observed, probably due to their relatively low content dispersed within the "soft" phase [8]. The neat HIPS exhibits a peak at 98.5°C, attributed to the T_g of polystyrene (PS), the major HIPS component. In the HIPS/TPU(65/35) blend, the two phases preserve their individual transitions, as is typical of immiscible polymer blends [11]; however, the T_g peak position of the TPU is shifted to a higher temperature (by ∼4°C), while the PS peak position is shifted to a lower temperature (by almost 10°C). The observed T_g shifts may be attributed to partial miscibility of the two polymers due to specific interactions between the polystyrene and polyurethane polymer chains. The polystyrene aromatic benzyl side groups can interact with the aromatic rings within the hard segments of the TPU forming some kind of π-bonds [12]. Another possible explanation for the T_g depression of the PS matrix can arise from some plasticization of polystyrene by low molecular weight fractions in the TPU.

By applying the simple Fox relationship [13], a phase composition of 5 wt% TPU within the PS phase corresponds to the observed T_g (of 88.5°C). Similarly, a phase composition of 5 wt% polystyrene within the TPU phase is predicted for the observed low T_g (of

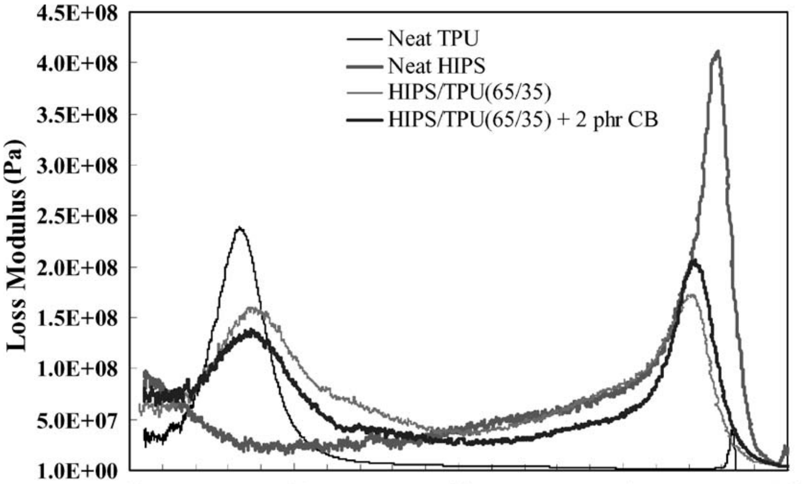

Figure 5 Loss modulus vs. temperature of neat and 2 phr CB-containing HIPS/TPU(65/35) blends and neat HIPS and TPU polymers. Compression molded specimens.

−41°C). However, it should be kept in mind that the HIPS/TPU blend is largely immiscible and thus, it is more likely that partial solubility of the polymers exists mostly at the interphase regions rather than in the bulk phases. Therefore, it is suggested that the microstructure of this blend consists of two conjugated PS and TPU phases and PS/TPU interphase regions. The formation of these boundary layers between the two polymers is further manifested by the good adhesion of the polystyrene matrix and the dispersed TPU phase as mentioned above.

The loss modulus curve of the 2 phr CB-containing HIPS/TPU(65/35) blend shows peaks at −42°C and 92°C, corresponding to the TPU phase and polystyrene matrix, respectively. Thus, the T_g peaks of the polystyrene matrix and TPU phase remain virtually unchanged, compared with the neat HIPS/TPU blend.

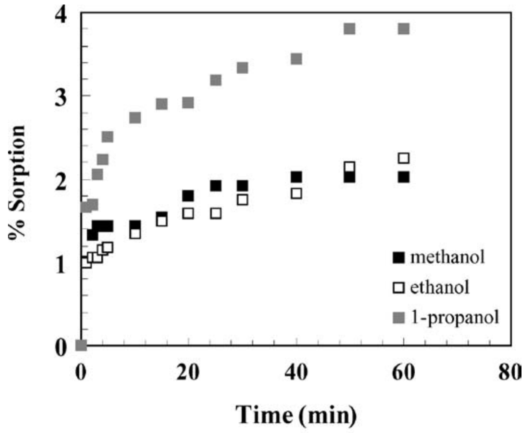

Figure 6 Sorption curves of HIPS/TPU(65/35) + 2 phr CB blend in different alcohols, calculated on original weight basis: (■)—methanol, (□)—ethanol and (▨)—1-propanol.

3.3. Sensing mechanism

It has been already established [7] that the mechanism governing the resistance increase in a CB-containing immiscible polymer blend characterized by a double-continuity structure is more complex than that of a single polymer system with CB.

In a single polymer/CB system the sensitivity is related to the sorption kinetics and partial dissolution in the polymeric matrix, both affected by the different characteristics of the sensed solvents (solubility parameter, polarity and molecular volume) [8]. However, immiscible polymer blends require additional considerations of interphase effects (e.g., size distribution of the dispersed phase, variation in shape of the dispersed particles, level of interaction etc.), which may complicate sorption and transport behaviour [14, 15]. Sorption of analyte molecules in such blends may occur through the HIPS matrix, the TPU phase, and the interphase regions that often may have higher sorption and diffusion coefficients than the adjoining individual phases [14]. The HIPS and TPU phases may sorb (and as a result swell) differently, depending on the characteristics of the specific liquid in contact. Sorption is affected by the affinity of the penetrating molecule to a given polymer and the penetrant molecular size and shape, as well as the state of the polymers, whether glassy or rubbery. Since the HIPS matrix is in its glassy state (at room temperature), significantly lower sorption rates are expected compared to the rubbery TPU phase [16]. Considering the affinity (expressed in terms of differences in either surface tension or Hilderbrand solubility parameter values), as HIPS has a lower surface tension than TPU (4×10^{-2} and 5.5×10^{-2} N/m, respectively) [17; BF Goodrich data], higher sorption values should be expected with the least polar alcohols. For the highly polar TPU phase, an opposite tendency should be expected. Considering the molecular volume, a lower volume (at the same polarity) should give rise to faster sorption kinetics and higher sorption values [18, 19]. Experimental sorption results for the HIPS/TPU(65/35) + 2 phr CB blend are depicted in Fig. 6. Significantly higher sorption values are observed for 1-propanol compared with the found similar values for the two other alcohols. At short exposure times, of interest for the sensing experiments, methanol is sorbed at a higher extent than ethanol. Dissolution experiments of the three studied alcohols have proven negligible weight losses. Hence, no partial dissolution of the HIPS/TPU blend takes place concurrently with the sorption process within the experimental time interval studied. Thus, the sorption results coincide with the observed resistance changes of the HIPS/TPU/CB filaments upon exposure to the various alcohols. Indeed, the HIPS/TPU/CB system depicts both the highest sorption level and the highest sensitivity toward 1-propanol, compared with the two other alcohols. As for methanol and ethanol, the discrimination ability of the HIPS/TPU/CB system is rather low in agreement with the sorption results.

The role of the interphase region and the adjoining individual HIPS and TPU phases in the overall permeation process should be considered. Sorption experiments for neat HIPS, the major component in the studied blend, in the three alcohols have demonstrated negligible sorption values. Since the sorption values for the immiscible HIPS/TPU are significant, it seems that the HIPS/TPU interphase region has a crucial role in the overall permeation process. It is suggested that this region has higher affinity toward 1-propanol, compared with the other two alcohols. This behavior stems from the surface tension of the interphase region, which may have a value between 40 to 55 dyne/cm, corresponding to HIPS and TPU, respectively. Moreover, this region can be more hydrophobic than its pure components as was previously found for a polyethylene oxide/polymethyl methacrylate (80/20) blend [20]. This result can further support the affinity of the interphase to 1-propanol, resulting in higher sorption extent (or faster sorption kinetics). Once sorbed in the interphase, the penetrating molecules are preferentially sorbed in the CB-containing rubbery TPU phase, selectively swelling the TPU dispersed particles. This swelling, as mentioned above, may affect the continuity of the dispersed phase and/or the continuity of the CB network within this phase. It should however be kept in mind that the swelling ability of the TPU particles, embedded within the stabilizing (glassy) HIPS matrix, is restricted.

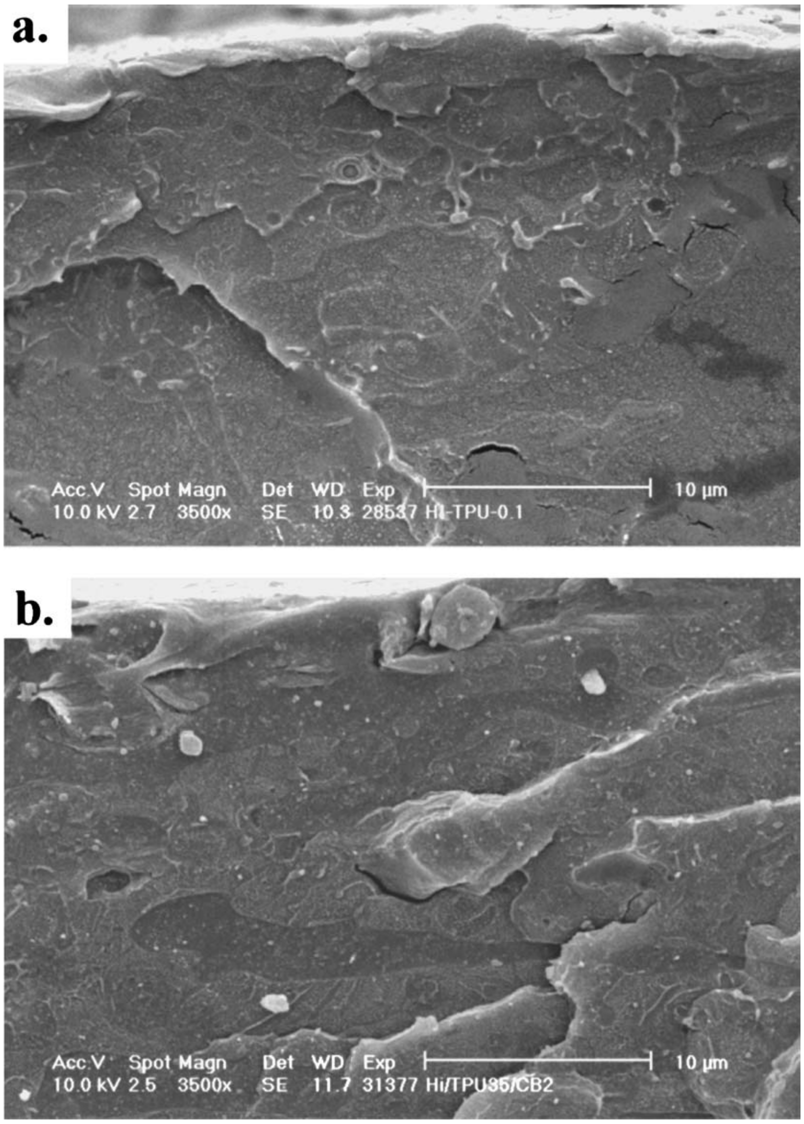

Figure 7 SEM micrographs of freeze fractured HIPS/TPU(65/35) + 2 phr CB filament (transverse to flow direction) (a)—before and (b)—after exposure to 1-propanol.

Fig. 7 displays the morphology of HIPS/TPU (65/35) + 2 phr CB filament (produced at an intermediate shear level, 60 s^{-1}) before and after exposure to 1-propanol and drying. The structure of the outer skin region (Fig. 7b) and the core region (not shown) of the filament seems to be unaffected by the liquid exposure. This result is rather surprising since the previously studied PP/TPU/CB filaments [7] exhibited significant interphase debonding upon exposure to the different alcohols. It was attributed to the preferential permeation of the polar liquids through the weak PP/TPU interfaces (debonding enhances liquid penetration by capillary flow along the interface accounting for the relatively high liquid concentration at the interfacial region). However, generally, interfacial adhesion existing between polymeric phases tends to retard the passage of solvent molecules [21]. Thus, the high interfacial adhesion of the HIPS matrix and the TPU dispersed phase, associated with the relatively low HIPS/TPU interfacial tension (compared with PP/TPU system), may slow down the permeation process through the interphase regions. Indeed, at short exposure times, lower sorption values are observed for the HIPS/TPU/CB system (see Fig. 6) compared with the PP/TPU/CB system. Moreover, it is suggested that the different nature of the two interphases, gradual in the HIPS/TPU blend vs. a sharp interphase in the PP/TPU system, results in the different resistivity behaviour to debonding processes.

Five consecutive immersion/drying cycles were performed in order to characterize the filaments' sensing reproducibility. The HIPS/TPU/CB filaments exhibit high reproducibility combined with relatively high sensitivity toward the studied solvents (see Fig. 2). Exceptional are the filaments exposed to 1-propanol. The sensitivity of these filaments tends to increase in the progressive cycles. Similar behaviour was previously observed in several single polymer/CB compounds i.e., ethylene vinyl acetate/CB and TPU/CB [3, 8]. These changes in resistance were accounted for by the occurrence of structural changes in the filaments (occurring mainly in the outer skin regions) due to solvent sorption/desorption during the immersion/drying cycles, respectively. However, in the present case, it is more likely that this behaviour stems from the accumulation of 1-propanol in the blend due to the short drying cycle. This suggestion is further verified by the partial reversibility (during the studied drying cycle) of filaments exposed to 1-propanol (see Fig. 2c). As suggested, during longer drying cycles of few hours, filaments exposed to 1-propanol returned to their initial resistance values. The reproducibility of the HIPS/TPU/CB sensor system may be attributed to the restricted swelling ability of the TPU particles imbedded in the intact, stabilizing HIPS matrix. The sensitivities displayed by the HIPS/TPU/CB filaments are significantly lower than those observed for the TPU/CB filaments. This result may be also attributed to the same argument of restricted swelling ability of the TPU particles in the blend.

3.3.1. Parameters affecting the sensitivity of the extruded filaments

3.3.1.1. Effect of matrix polymer nature. Immiscible CB-containing PP/TPU blends were previously studied as sensing materials [7]. In these blends, PP serves as a semicrystalline matrix and TPU as a soft dispersed amorphous phase. The 2 phr CB-containing PP/TPU filaments exhibited higher sensitivity i.e., relative resistance changes, upon exposure to methanol, ethanol and 1-propanol, compared with the present HIPS/TPU/CB system. This behaviour was observed for filaments produced at all shear rate levels. For example, PP/TPU/CB filaments produced at a high shear rate level of 600 s^{-1} exhibited a relative resistance value of $\sim$23 upon exposure to 1-propanol compared with only 4.6 observed for the HIPS/TPU/CB filaments (initial resistance values for the HIPS/TPU/CB and the PP/TPU/CB filaments were comparable). Furthermore, while the PP/TPU/CB system tends to reach a constant level of resistance during the exposure cycle, the resistance of the HIPS/TPU/CB system gradually increases during the exposure cycle and does not reach a plateau during the studied exposure time. Thus, the observed rate of response of the PP/TPU/CB system is higher than that of the HIPS/TPU/CB system. This behaviour can be attributed to two different factors: (i) the T_g of the matrix polymer and (ii) the quality and the quantity of the interphase between the matrix and the dispersed polymer phase. In the HIPS/TPU system the PS matrix is in the glassy state (below T_g) at room temperature, whereas in the PP/TPU system the semicrystalline PP matrix amorphous regions are in the rubbery state. Thus, it is expected that the PP system will exhibit somewhat higher sorption and diffusion coefficients. Furthermore, the swelling ability of the TPU phase is more restricted in the HIPS/TPU system due to the glassy nature of the PS matrix. As for the quality of the interphase, the HIPS/TPU system exhibits higher interfacial adhesion compared with the PP/TPU system, retarding the passage of solvent molecules.

3.3.1.2. Effect of dispersed phase nature. It is interesting to compare the sensing properties of HIPS/EVA/CB [3] and the HIPS/TPU/CB systems, since the dispersed phase in both, TPU and EVA copolymers, are thermoplastic elastomers. Negligible resistance changes were observed for HIPS/EVA(85/15) + 4 phr CB filaments (produced at intermediate shear rate level) exposed to methanol, while the HIPS/TPU/CB system exhibited relative resistance changes of more than 4 times (Fig. 2a). The enhanced sensitivity of the HIPS/TPU/CB filaments to methanol is related to the effective CB content and the different characteristics of the dispersed copolymers. In the HIPS/EVA/CB system, the high CB content (4 phr within 15 wt% EVA), further concentrating in the amorphous intercrystallite regions, enhances the formation of a high-quality CB network. In the HIPS/TPU/CB system, the lower CB content (only 2 phr) combined with the preferential localization of CB particles within the entire amorphous TPU phase (35 wt% of the blend) results in a decreased effective CB content and thus a "fragile" network quality. The dense CB network is less likely to be affected by the swelling processes occurring during the analyte sorption. Another factor affecting sensitivity stems from the difference in sorption of solvents and swelling ability of the different dispersed phases. The crystalline regions in the EVA phase are inaccessible to penetrants, hence, they act as excluded volumes for the sorption process and as impermeable barriers for the diffusion process. Furthermore, these crystallites also restrict the swelling of the amorphous phase. Thus, the lower sorption and swelling ability of the EVA phase compared with TPU also reduce the sensitivity level of the blend to a given analyte.

4. Conclusions

– Structural and electrical double-percolation is implemented in the HIPS/TPU/CB system through the formation of a co-continuous TPU phase in which CB particles form chain-like network structures. Furthermore, DMTA and SEM studies suggest a blend microstructure consisting of two conjugated PS and TPU phases and PS/TPU interphase regions.

– The HIPS/TPU/CB filaments exhibit selective sensitivity to a homologous series of alcohols. Significant resistance reproducibility and recovery behavior combined with relatively high sensitivity levels towards the studied alcohols were displayed.

– The different selectivities and sensitivities exhibited by the HIPS/TPU/CB system compared with those exhibited by the reference TPU/CB and HIPS/CB systems, suggest that the sensing mechanism of the immiscible blend is different from that of the corresponding individual components with CB.

– The HIPS/TPU interphase region has a crucial role in the overall permeation process, determining the specific selectivity of the blend toward the studied analytes. Once sorbed by the interphase, the penetrating molecules are preferentially sorbed in the CB-containing rubbery TPU phase, selectively swelling the TPU dispersed particles. This swelling affects the continuity of the dispersed phase and/or the continuity of the CB network within this phase, resulting in the observed resistance increase.

– Additional main effects of matrix and dispersed polymers nature on the sensing performance of CB-containing immiscible polymer blends are as follows: (i) the T_g of the blend polymers; (ii) the quality and the quantity of the interphase between the matrix and the dispersed polymer phase; (iii) the quality of the CB network, as determined by the actual CB local content and the nature of the polymer phase it is preferentially located in.

Acknowledgments

The authors are grateful to the U.S.—Israel Binational Science Foundation (BSF) for partial support of the sensors project. E. Segal gratefully acknowledges the generous financial support of the Levi Eshkol scholarship from the Israel Ministry of Science.

References

1. B. J. DOLEMAN, R. D. SANNER, E. J. SEVERIN, R. H. GRUBBS and N. S. LEWIS, *Anal. Chem.* **70** (1998) 2560.
2. S. SRIVASTAVA, R. TCHOUDAKOV and M. NARKIS, *Polym. Eng. Sci.* **40** (2000) 1522.
3. M. NARKIS, S. SRIVASTAVA, R. TCHOUDAKOV and O. BREUER, *Synth. Metals* **113** (2000) 29.
4. O. BREUER, R. TCHOUDAKOV, M. NARKIS and A. SIEGMANN, *J. Appl. Polym. Sci.* **64** (1997) 1097.
5. *Idem.*, *ibid.* **74** (1999) 1731.
6. *Idem.*, *ibid.* **73** (1999) 1655.
7. E. SEGAL, R. TCHOUDAKOV, M. NARKIS and A. SIEGMANN, *J. Polym. Sci. Part B: Polym. Phys.* **41** (2003) 1428.
8. *Idem.*, *Polym. Eng. Sci.* **42** (2002) 2430.
9. J. R. LI, J. R. XU, M. Q. ZHANG and M. Z. RONG, *Macromol. Mater. Eng.* **288** (2003) 103.
10. F. GUBBELS, S. BLACHER, E. VANLATHEM, R. JEROME, R. DELTOUR, F. BROUERS and PH. TEYSSIE, *Macromoleules* **28** (1995) 1559.
11. L. E. NIELSEN and R. F. LANDEL, "Mechanical Properties of Polymers and Composites" (Marcel Dekker Inc, New York, 1994) p. 197.
12. P. S. THEOCARIS and V. KEFALAS, *J. Appl. Polym. Sci.* **44** (1991) 3059.
13. W. J. MACKNIGHT, F.E. KARASZ and J. R. FRIED, in "Polymer Blends," edited by D. R. Paul and S. Newman (Academic Press Inc., New York, 1978) p. 189.
14. C. E. ROGERS, in "Polymer Permeability," edited by J. Comyn (Elsevier Appl. Sci., London, 1985) p. 11.
15. M. R. KAMAL, I. A. JINNAH and L. A. UTRACKI, *Polym. Eng. Sci.* **24** (1984) 1337.
16. Y. M. SUN, *Polymer* **37** (1996) 3921.
17. S. WU, "Polymer Interface and Adhesion" (Marcel Dekker Inc., New York, 1982) p. 184.
18. S. LEE and K. S. KNAEBEL, *J. Appl. Polym. Sci.* **64** (1997) 455.
19. G. GUERRICA-ECHEVARRIA, J. I. EGUIAZABAL and J. NAZABAL, *J. Macromol. Sci.-Phys.* B **39** (2000) 441.
20. A. ELEBERAÏCHI, A. DARO and C. DAVID, *Euro. Polym. J.* **35** (1999) 1217.
21. S. C. GEORGE, G. GROENINCKX, K. N. NINAN and S. THOMAS, *J. Polym. Sci. Part B: Polym. Phys.* **38** (2000) 2136.

Received 6 November 2003
and accepted 30 April 2004