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# Conductive Composite Materials of Polyethylene and Polypyrrole with High Modulus and High Strength

*Dan Zhu,*[1] *Yuezhen Bin,*[1] *Kumiko Oishi,*[1] *Yasuyuki Fukuda,*[2]
*Takahiko Nakaoki,*[2] *Masaru Matsuo**[1]

[1] Department of Textile and Apparel Science, Faculty of Human Life and Environment, Nara Women's University, Nara 630-8263, Japan
E-mail: m-matsuo@cc.nara-wu.ac.jp
[2] Department of Material Chemistry Science, Faculty of Science and Technology, Ryukoku University, Ootsu City, 520-2194, Japan

**Summary**: Composite films of polyethylene (PE) and polypyrrole (PPy) were prepared by polymerization of PPy on an ultradrawn polyethylene film with high modulus and high strength in ferric chloride ($FeCl_3$) aqueous solution. The electrical conductivity of the composite film was found to be related to the polymerization conditions, such as polymerization temperature, polymerization time, the concentration and the oxidation potential of the $FeCl_3$ solution. Scanning electron microscopy, FTIR and $^{13}C$ NMR spectra were used to elucidate the morphological and structural variations of PPy prepared under different conditions, which lead to the differences in the electrical properties of the resultant composite films. The best electrical conductivity of the composite was about 5.5 S/cm for the film prepared under optimum conditions. The Young's modulus and the tensile strength reached 80 GPa and 3.2 GPa, respectively, which indicated the successful production of a conductive polymer with high strength and high modulus.

**Keywords**: composite; electrical conductivity; high modulus; high strength; polyethylene; polypyrrole

## Introduction

Multifunctional polymers with a combination of functions such as nonlinear optical response, piezo- and pyro-electric effects, photoconductivity and electric conductivity have received

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much attention in the industrial field as special materials. They play a critical role in the new development of advanced materials having wide applications in telecommunications, data communications, information storage and other areas.[1] The polymerization method of polypyrrole (PPY) reported by Italian chemists[2] has been improved by Kanazawa et al and Diaz et al. [3-5]; a modification of the electrochemical technique was used and good results have been obtained.

PPy has a higher durability in air than other conjugated conducting polymers such as polyacetylene, and has advantages as an industrial material. The weakness of PPy lies in its mechanical properties. Recent research of polypyrrole has concentrated on improving its conductivity, processability and mechanical properties. This has been done by, for example, polymerizing pyrrole onto a supporting surface such as polyvinyl alcohol[6] or polymer-coated electrodes.[7] Composites of PPy and olefins such as polypropylene have also been produced by melt mixing, but the resultant mechanical property was not very good.[8]

On the other hand, high modulus and high strength polyethylene fibers and films were easily prepared by gelation/crystallization from dilute solutions by using ultrahigh molecular weight polyethylene (UHMWPE). This work have been done by Smith et al.[9,10], Matsuo[11-13] et al. and Kanamoto et al.[14,15]. By controlling the concentration of UHMWPE ($\overline{M}_v$=6$\times 10^6$) solutions, the dry gel films could be elongated up to 400 fold and the Young's modulus reached 216 GPa,[12] which is close to the crystal lattice modulus along the chain axes corresponding to the ultimate value of polyethylene.

This paper is concerned with the preparation of composite materials of ultradrawn PE with excellent mechanical properties and PPy with good electrical features. The polymerization of pyrrole in an oxidative solution was allowed to take place on the surface of an ultradrawn

PE film as substrate. The polymerization conditions such as temperature, time, oxidation potential and the concentration of the oxidative agent were optimized in extensive preliminary experiments. The characteristics of the composite film were measured by wide angle X-ray diffraction (WAXD), small angle X-ray scattering (SAXS), scanning electron microphotography (SEM), different scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR).

## Experimental

**Sample Preparation:** The polyethylene samples used in this experiment were UHMWPE (Hercules 1900/90189) with a viscosity-average molecular weight ($\overline{Mv}$) of $6\times10^6$. The solvent was decalin. The concentration of UHMWPE chosen was 0.4 g/100ml decalin, which is the optimum concentration ensuring the greatest draw ratio of UHMWPE films with $\overline{Mv} = 6\text{x}10^6$ [11, 12]. Decalin solutions were prepared by heating a well-blended polymer-solvent mixture at 135 ℃ for 40 min under nitrogen. The solution was stabilized with 3 wt% of an antioxidant (di-t-butyl-p-cresol) against UHMWPE. The hot homogenized solution was quenched to room temperature by pouring it into an aluminum tray, thus generating a gel. The decalin was evaporated from the gels under ambient conditions. The resulting dry gel film was vacuum-dried for 24 h to remove any residual trace of decalin, and then elongated up to the desired fold at 135 °C under nitrogen. The thickness of the ultradrawn PE film was in the range of 3~20 μm. A more detailed method has been described elsewhere.[16,17] The ultra-drawn films were washed in ethanol and dried before being used as substrates.

The electric conductivity of PPy polymerized under electric field is well known to increase with decreasing polymerization temperature. This well-known method, cannot however be applied to the polymerization on polyethylene as substrate, since polyethylene is a typical insulator. Accordingly, the ultra-drawn polyethylene film was dipped in purified pyrrole monomers, and transferred into an aqueous $FeCl_3$ solution. The latter was used as an oxidant, in which $Cl^-$ acts as a dopant anion to PPy.[18] After the polymerization, the film was washed with distilled water to remove the excess oxidant, and then with ethanol and acetone to remove the unreacted monomers and oligomers. The resultant film was then dried under vacuum at room temperature for 24 h.

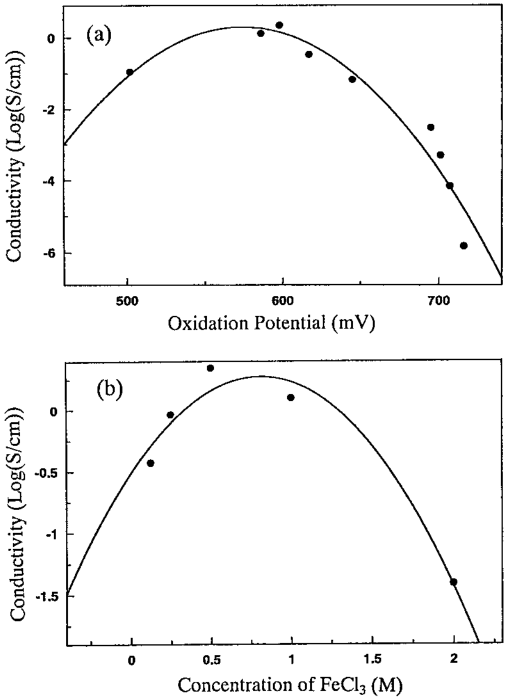


Figure 1. Electric conductivity of the composites as a function of (a) oxidation potential of the solution, in which PPy was polymerized at 20 ℃ for 3 hr in the 0.5 M $FeCl_3$ solution, (b) $FeCl_3$ concentration in the solution with oxidation potential of 600 mV.

To obtain the maximum value of electric conductivity of the PE-PPy composite, the optimum polymerization conditions of PPy on the substrate of PE with $\lambda = 100$ must be determined by controlling four parameters; polymerization temperature, polymerization time, concentration of $FeCl_3$ solution, and the oxidation potential of the solution, apart from the well-known best polymerization conditions of PPy under electric field. According to the Nernst's equation[19], indicating that oxidant potential decreases as $Cl^-$ increases in a $FeCl_3$ solution, a solution with the desired initial oxidation potential was prepared by adjusting the

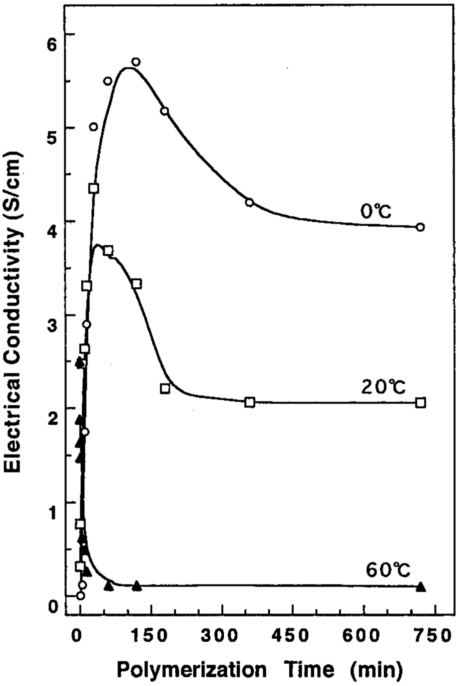


Figure 2. Electric conductivity of the composites vs. polymerization time of PPy at 0, 20, and 60 °C.

amount of $Cl^-$ in the solution, namely by adjusting the proportion of HCl and $H_2O$, before the polymerization and the oxidation potential was measured with a digital pH meter, model HM-20E, provided by TOA Electronics Ltd., Japan. First, polymerization temperature and polymerization time, and the concentration of the solution were fixed to be 20 ℃, 3 h, and 0.5 M. The oxidation potential of the solution was changed from 500 to 720 mV. Figure 1(a) shows the results. The conductivity of the resultant composite becomes the maximum at about 600 mV.

In the next step, the conductivity of the composite was obtained as a function of the concentration of $FeCl_3$ in the solution with an oxidation potential of 600 mV. The concentrations were varied in the range from 0.1 to 2 M and the polymerization temperature and the polymerization time were also fixed at 20 ℃ and 3 h, respectively. Figure 1(b) shows the change in electric conductivity against $FeCl_3$ concentration. The electric conductivity of the composite was found to be maximum at 0.5 M concentration. By using the solution with 0.5 M concentration and with oxidation potential of 600 mV, the composites were prepared by changing the other two parameters, polymerization temperature and polymerization time.

Figure 2 shows the electric conductivity of the composites against polymerization time at 0, 20, and 60 °C. This experiment was carried out to check the relationship between the amounts of polymerized PPy on polyethylene film and the electric conductivity. In the initial stage, the electric conductivity increases drastically and reaches a maximum value, indicating a rapid formation of conductive paths. The further increase in polymerization time, beyond each maximum value of conductivity for the three composites, causes a drastic decrease in conductivity and it tends to level off. This tendency is most considerable at 60

°C. The decrease of conductivity of PPy is thought to be due to change in the oxidation potential of the solution with increasing polymerization time. Interestingly, the maximum values and the time elapsed prior to arriving at the maximum are sensitive to the polymerization temperature. Namely, the magnitude of electric conductivity is highest at 150 min, when the polymerization is done at 0 °C. This phenomenon shall be discussed later in relation to the temperature dependence of the chemical structure of PPy, as determined by FTIR and $^{13}$C NMR spectra.

**Characterization of UHMWPE-PPy composites:** The electrical conductivity of the drawn films was measured in the stretching direction by using a two-terminal method at room temperature or in the temperature range from -150 to 220 °C.

The DSC measurements were done with an EXTRA-6000, furnished by Seiko Instrument Inc. Sample sizes of 1 mg were used, under nitrogen, and the heating rate was 10 ℃/min. An FTIR-8300 from Shimadzu was used to record the infrared spectra of the composite films.

X-ray measurements were carried out with a 12-kW rotating-anode X-ray generator (Rigaku RAD-rA). Monochromatic CuK$\alpha$ radiation (wavelength of 0.154nm) was used. WAXD patterns were obtained with a flat camera and SAXS intensity distribution in the meridional direction was detected with a position sensitive proportional counter (PSPC). Corrections of X-ray scattered intensity were made for air scattering, polarization and absorption.[20]

SEM photographs were taken with a HITACHI-X650, with a working voltage of 20 kV and magnification 1000.

The temperature dependence of the dynamic tensile modulus was measured with a visco-elastic spectrometer (VES-F), obtained from Iwamoto Machine Co., Ltd., at a fixed frequency of 10Hz over the temperature range of -150-300 °C. The Young's modulus and tensile strength were measured at room temperature with a Tensilon / STM-H-500BP.

## Results and Discussion

Figure 3 shows the SEM photographs of the surfaces of the PE-PPy composites prepared at the indicated polymerization temperatures and polymerizetion times. The number of PPy particles on the surface increases and the particle size becomes bigger with increasing temperature and time. After 10 sec, the substrate's surface is covered by a large amount of PPy particles when the polymerization was done at 60 °C. Judging from the results in Fig. 2, it may be expected that the electric conductivity of PPy is sensitive to polymerization temperature. This phenomenon is thought to be due to the dependence of the chemical structure of Ppy on polymerization temperature. This shall be discussed later when the FTIR and $^{13}$C NMR spectra are considered.

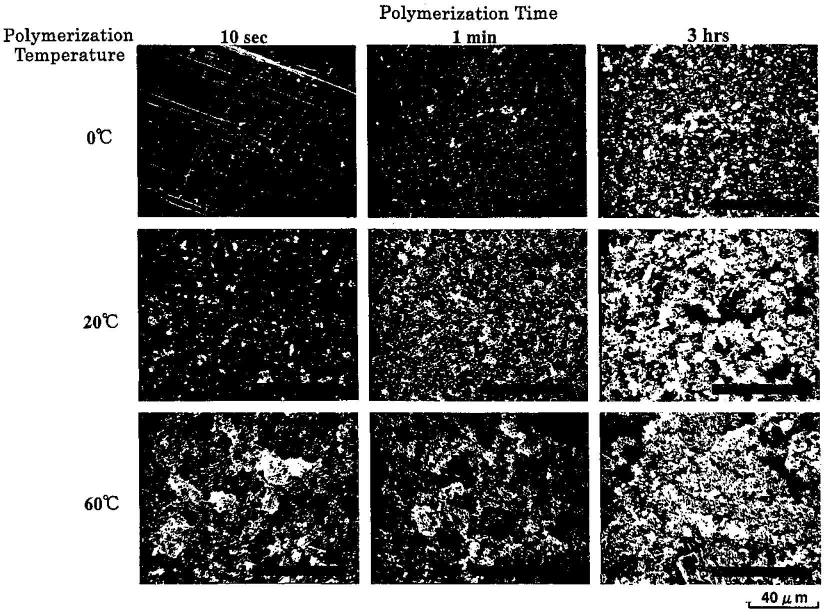


Figure 3. SEM photographs of the surface of PE-PPy composites, in which PPy was polymerized at the indicated polymerization temperature and polymerization time.

Table 1 The density of films and the weight fraction of PPy in the PE/PPy blend films at the different draw ratios

| | | Draw ratio λ (fold) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1 | | 50 | | 100 | | 200 | |
| | | Density ($g/cm^3$) | Weight fraction (%) | Density ($g/cm^3$) | Weight fraction (%) | Density ($g/cm^3$) | Weight fraction (%) | Density ($g/cm^3$) | Weight fraction (%) |
| PE | | 0.9768 | – | 0.9858 | — | 0.9933 | — | 0.9998 | — |
| PE-PPy | 0℃ | 0.9833 | 0.50 | 1.0821 | 27.78 | 1.0522 | 37.27 | 1.0497 | 57.25 |
| | 20℃ | 0.9846 | 0.69 | 1.2180 | 34.51 | 1.1030 | 63.12 | 1.0993 | 58.04 |
| | 60℃ | 0.9931 | 3.59 | 1.2138 | 52.46 | 1.1754 | 65.81 | 1.1199 | 64.32 |

Here we must emphasize that the PPy particles that over-lapped on the surface could be removed by soft paper, since most of polymerized PPy particles were on the surface of PE, they had not penetrated into the interior of PE film, as shown in Fig. 3, at elevated polymerization temperature. This is important, to estimate the amount of PPy that penetrated into cracks between oriented PE fibrils, in measuring electric conductivity. Therefore the specimens with no overlapped particles on the surface were used as test specimens in the following experiments. Table I lists the weight fractions of PPy in PE-PPy composites prepared by the polymerization of PPy at 0, 20, and 60 °C after removing the overlapped particles. The polymerization time was set to be 2 h, assuring the highest conductivity of PPy polymerized at 0 °C. To check the draw ratio dependence on the conductivity of the composites, PE films with different draw ratio were used as substrates.

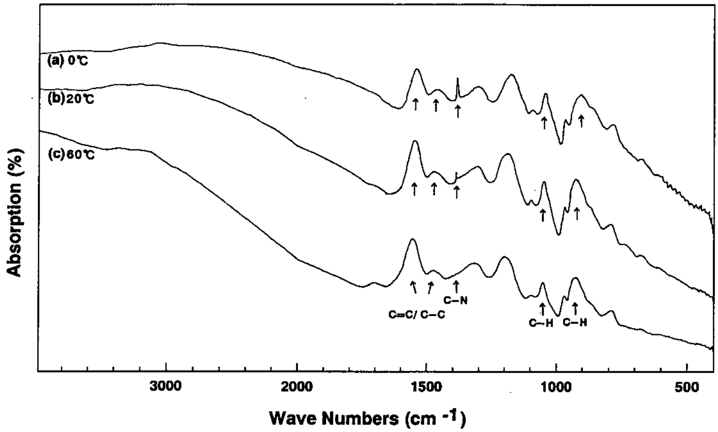
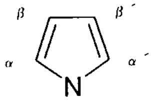


Figure 4. FTIR spectra measured for PPy polymerized at 0, 20, and 60 °C.

The weight fraction was calculated by the weight of the film before and after the polymerization. The PPy fraction of the composite becomes higher as the draw ratio of PE as substrate becomes higher. This is because of the decrease of film thickness with increasing draw ratio. The cross-section area was calculated from the density, measured using a pycnometer, with toluene and carbon tetrachloride as solvents. Direct measurement of the film thickness using a micrometer was impossible, since the thickness was too thin to be estimated accurately. Accurate values of the cross-section area are very important to estimate Young's modulus and tensile modulus of the composite films.



Returning to Fig. 2, it is seen that the electric conductivity of PPy is lower with increasing polymerization temperature, although the amount of polymerized PPy increases. To explain this phenomenon, FTIR spectra were measured for PPy polymerized at 0, 20 and 60 °C. Figure 4 shows the results. The N– H or C– H feature absorption is invisible from 1600 to 4000 $cm^{-1}$, since they are masked by the tail of the 1 eV peak generally formed due to the doping.[21] In the region from 1600 to 400 $cm^{-1}$, the vibrations of pyrrole ring appear, i.e. at 1540 and 1470$cm^{-1}$, associated with the C– C and C=C stretching, and at 1384 $cm^{-1}$, associated with C– N stretching. According to the quantum chemical calculation by Tian et

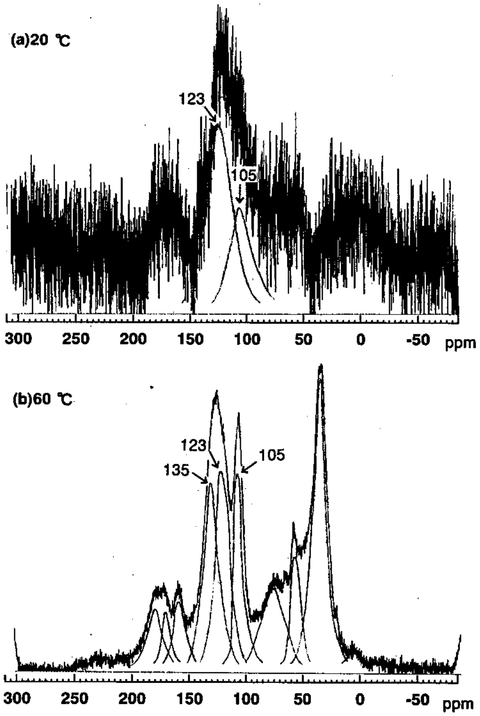


Figure 5. $^{13}C$ NMR spectra of PPy polymerized at 20 and 60 °C.

al.[22, 23], the dopant molecules will lead to the abovementioned bands being selectively and strongly enhanced. In our IR spectra, the PPy polymerized at lower temperature is considered to be of higher doping degree. Following Tian and Zerbi[21-24] the ratio of the absorption intensity of 1550 and 1470 cm$^{-1}$ ($I_{1550}/I_{1470}$) was reported to be inversely proportional to the extent of delocalization, namely, the conjugated length along the polymer chains. In Figure 4, the $I_{1550}/I_{1470}$ is 2.6, 3.0, and 4.0 for the PPy prepared at 0, 20 and 60 °C, respectively, indicating that PPy synthesized at lower temperature has a lower $I_{1550}/I_{1470}$ value. This means that PPy polymerized at the lower temperature has longer extended conjugation and less defect sites in the chain than the other two.

The solid $^{13}$C NMR spectra for the PPy polymerized at 20 and 60 °C are shown in Figure 5. The conductive samples were dispersed by grinding together with salt powder before setting into the sample rotor. The spectrum of PPy polymerized at 0 °C could not be obtained, while that at 20 °C contained much noise. These phenomena are attributed to electric discharge in the magnetic field, as frequently occurs with conducting materials. Both spectra 5(a) or 5(b) show a very broad asymmetric peak shifted downfield, compared with neutral PPy.[25] The major peaks at 123 and 105 ppm downfield from tetramethylsilane (TMS) correspond to the α- and β-carbons of the pyrrole monomer, respectively, which appear normally at 117 and 108 ppm relative to TMS.[21, 26] The peak at 135 ppm may indicate the presence of some non α− α linkages, such as α− β linkage or chain end groups. The PPy synthesized at 20 °C shows more linkage of α carbon than PPy synthesized at 60 °C. This is in good agreement with the structural analysis for PPy, indicating that the higher conductivity PPy has more α− α linkages. [21] The defect-forming reaction with high activation energy is predominant in comparison with the desired α− α linkages reaction as the polymerization temperature increases. Since the defect-forming reaction causes cut-off spots in the conjugating chain and induces irregularity in molecular structure, PPy polymerized at higher temperatures leads to low electric conductivity.

Figure 6 indicates the temperature dependence of the electric conductivity of PE ( $\lambda = 200$) and PE/PPy ( $\lambda = 200$) composite films prepared by using PPy polymerized at 0, 20 and 60 ℃. The polymerization time was fixed at 2 h (based on the results in Fig. 2). Conductivity measurements of the composites were done in temperature range from –150 to 150 °C in air. The conductivity of the composite is much higher than that of the PE film. As shown in Fig. 2, the conductivity of the composite film prepared at polymerization temperature 0 °C is higher than that of the samples prepared at the other polymerization temperatures, 20 and 60 °C.

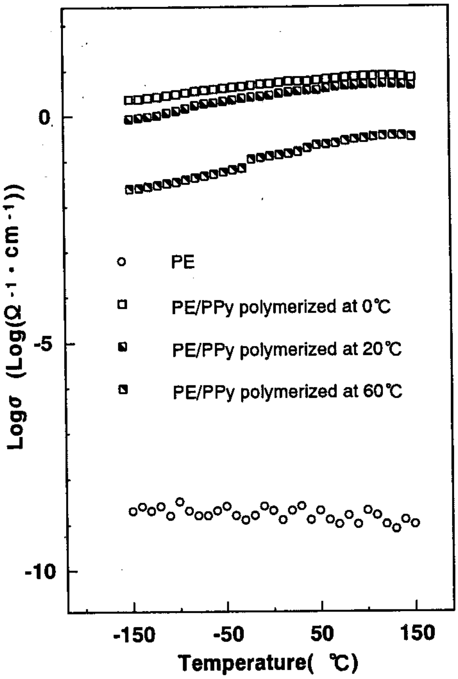


Figure 6. Temperature dependence of electric conductivity of PE and PE/PPy composite films prepared by using PPy polymerized at 0, 20, and 60 °C.

The increase in conductivity with temperature is very small. This means that the electrical property of the composite film is stable in air in the temperature range from –150 to 150 °C. Incidentally, the draw ratio of the composite films is almost independent of the electric conductivity in the given temperature range. Then we shall discuss the mechanical properties of the composite films as a function of draw ratio.

Figures 7 show the Young's modulus and the tensile strength for PE films and PE/PPy composite films.

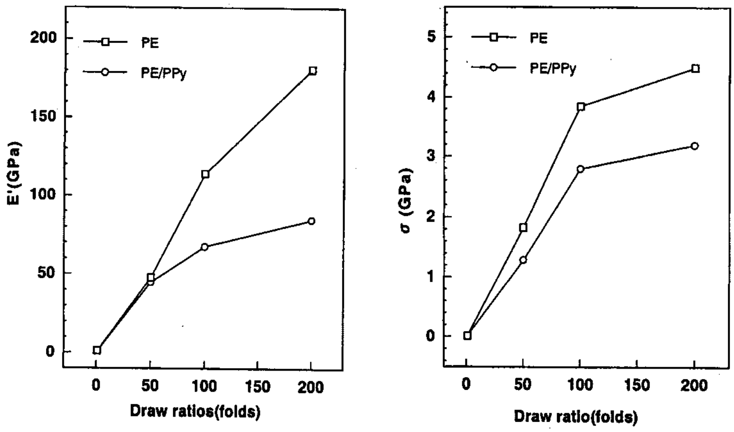


Figure 7. Young's modulus and tensile strength of PE films and PE/PPy composite films as a function of draw ratio.

The polymerization of PPy was carried out in the $FeCl_3$ solution at 0 °C for 2 hrs, which corresponds to the optimum condition as discussed before. It is clear that the higher the draw ratio of PE as substrate, the higher the Young's modulus and the tensile strength of the

PE/PPy composite film. For the PE film with 200 folds, Young's modulus and tensile strength reach 180 and 4.5 GPa, respectively, while Young's modulus and tensile strength of the corresponding composite film reach 80 GPa and 3.2 GPa. The drastic decrease is due to the fact that there is no contribution of PPy to the mechanical properties, Young's modulus and tensile strength and this is attributed to the increase in the cross section area of the composite films, as shown in Table 1. We must emphasize that the Young's modulus of the composites is practically the same as that of drawn PE homo-polymer films within the experimental error. Because, Young's modulus of PPy is negligible in comparison with the Young's modulus of PE and the introduction of PPy only increases the cross section area of the composite.

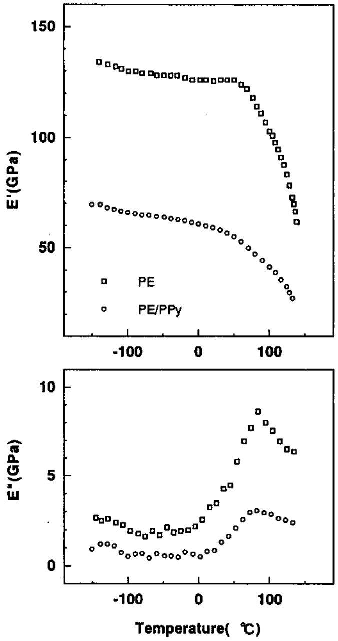


Figure 8. Temperature dependence of the storage and loss moduli of the PE film and PE/PPy composite film at $\lambda$ =100.

Figure 8 shows the temperature dependence of the storage and the loss moduli of the PE film and PE/PPy composite film with λ = 100. The polymerization temperature and polymerization time were selected to be 0 ℃ and 2 hrs, respectively. The decrease in the storage modulus for the composite film compared with that of the PE film is also due to the increase in the cross section area by the introduction of PPy as discussed above. The loss modulus showed the α-dispersion peak associated with crystal dispersion[27-28] of PE appears around 90 °C for both the specimens. The β–mechanism, which appears around – 30 °C – 50 °C generally for melt PE films and is associated with the amorphous dispersion, is not observed for the composite because of high crystallinity of the ultradrawn PE matrix. Accordingly, the temperature dependence of the storage and loss moduli indicates that compositing of PPy caused no damage to the crystalline within PE substrate.

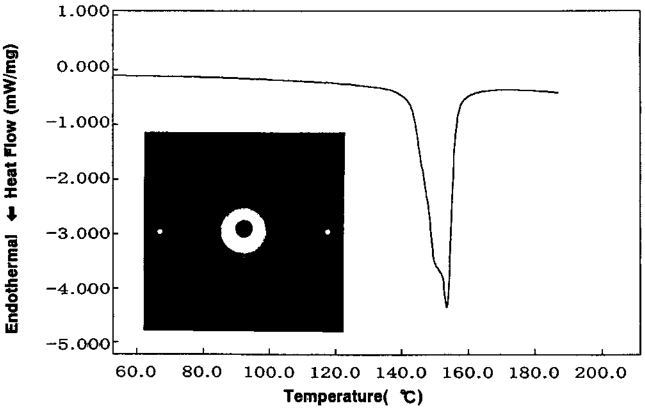


Figure 9. DSC and X-ray diffraction pattern for PE/PPy composite (λ =100).

To confirm this conclusion, DSC and X-ray diffraction measurements were done for the PE film and PE/PPy composite film with λ= 100. Figure 9 shows the results. DSC curve shows an endotherm peak at 152 °C for the PE/PPy composite film. The curve with same profile was also observed for the ultradrawn PE film.[16] The WAXD pattern shows strong equatorial reflecting spots from the (110) plane, as observed for the ultradrawn film, indicating a high degree of orientation of the c-axes with respect to the stretching direction. Judging from the WAXD pattern, the introduction of PPy particles causes no effect on the high orientation of the PE crystallites, since PPy is of extremely poor crystalline, as reported for all forms of PPy so far.

WAXD pattern and SAXS patterns were taken from edge view for the undrawn composite film, although they are not shown in this paper. The reflection from (110) and (200) planes showed the preferential orientation of the c-axes perpendicular to the film surface from the gelation process. The SAXS pattern showed the scattering maxima in the meridional direction, indicating that the crystal lamellae were oriented with their flat faces parallel to the film surface. The both patterns are the same as the PE undrawn films prepared by gelation/crystallization from solutions.

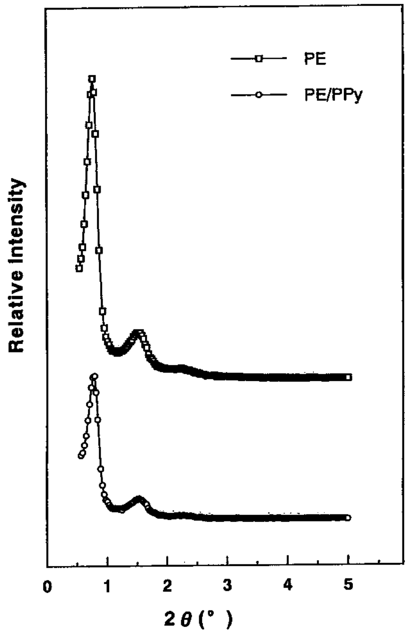


Figure 10. SAXS intensity distribution as a function of twice Bragg angle (2$\theta$) in the direction parallel to the film surface for the undrawn PE and PE/PPy .

In order to obtain the precise information, SAXS intensity in the meridional direction parallel to the film surface (end view) was observed as a function of twice the Bragg angle (2 $\theta$ ) by PSPC system for the undrawn PE and PE/PPy composite films. The result was shown in Figure 10. Typically, undrawn UHMWPE dry gel film shows a SAXS profile reflecting alternating lamellae with an identity period. [29] The three meridional scattering maxima indicate that the film is composed of highly oriented crystal lamellae with their faces parallel to the film surface. For the PE/PPy composite film, the strength of the scattered maxima become indistinct, the peaks can be observed at the same twice the Bragg angle. Thus it turns out that the orientation of the crystal lamellae with their faces parallel to the film surface causes no significant by the introduction of PPy particles. The change in the intensity is thought to be due to the absorption of X-ray by PPy

## Conclusion

A conductive PE/PPy composite film was synthesized by chemical polymerization of a pyrroles monomer on an ultradrawn PE substrate. The optimum reaction conditions, were the following: polymerization temperature 0 °C, polymerization time < 2 h, concentration of $FeCl_3$ in the aqueous solution 0.5 M, and oxidation potential was about 600 mV. The Young's modulus and tensile strength of the resultant composite film prepared from PPy synthesized under these optimum conditions reached 80 GPa and 3.2 GPa, respectively, and the electrical conductivity reached 5.5 S/cm at room temperature. No damage to the oriented PE substrate by the introduction of Ppy was confirmed. This lead to the successful production of conductive polymers with high modulus and high strength.

[1] J. P. Riggs, A. Harris, and J. B. Stamatoff, Frontiers of Polymer Research, P. N. Prasad and J. K. Nigam, Ed., Plenum Press, New York, **1991.** p.27-44.

[2] G. B. Street, Handbook of Conducting Polymers, T. A. Skotheim, Ed., New York, M. Dekker, **1986,** p.265-291.

[3] K. Kanazawa, et al., *Synth. Met.* **1979,** *1*, 329.

[4] M. Salmon, K. Kawakawa, A. F. Diaz, and M. Krounbi, *J. Polym. Sci. Polym. Lett. Ed.,* **1982,** *20,* 187.

[5] A. Diaz, and B. Hall, *IBM J. Res. Dev.* **1983,** *27(4)* 342.

[6] S. E. Lindsey and G. B. Street, *Synth. Met.*, **1984,** *10,* 67.

[7] O. Niwa and T. Tamamura, *J. Chem. Soc., Chem. Commu* , **1984,** *13,* 817.

[8] M. Omastova, I. Chodak, J. Pointech, *Synth. Met.* **1999,** *102,* 1251.

[9] P. Smith, P. J. Lemstra, B. Kalb, A. J., Pennings, *Polym Bull*, **1979,** *1* 733.

[10] P. Smith, P. J. Lemstra, J. P. L. Pijpers, A. M. Kiel, *Colloid & Polym. Sci.*, **1981,** *259,* 1070.

[11] M. Matsuo, K. Inoue, N. Abumiya, *Sen-I Gakkaishi*, **1984,** *40*, T275.

[12] M. Matsuo, C. Sawatari, *Macromolecules*, **1986,** *19*, 2028.

[13] C. Xu, Y. Agari, M. Matsuo, *Polym J.*, **1998,** *30(5)* 372.

[14] T. Kanamoto, A. Tsuruta, K. Tanaka, M. Katada, R. S. Portor, *Polymer J.*, **1983,** *15,* 327.

[15] T. Kanamoto, T. Ohama, K. Tanaka, M. Takeda, R. S. Portor, *Polymer* **1987,** *28*, 1517.

[16] T. Ogita, R. Yamamoto, N. Suzuki, F. Ozaki, M. Matsuo, *Polymer* **1991,** *31*, 882.

[17] M. Matsuo, C. Sawatari, M. Iida, M. Yoneda, *Polymer J.*, **1985,** *17,* 1197.

[18] A. Techagumpuch, Frontiers of Polymer Research, P. N. Prasad and J. K. Nigam, Ed., Plenum Press, New York, **1991,** p351-357.

[19] C. X. Fu, W. X. Shen and T. Y. Yao, *Physical Chemistry*, High Education Press: **1993**, p 505.

[20] G. D. Zhou, L. Y. Duan, The Structural Chemistry, Beijing Uni. Press, **1995**.

[21] J. E. Mark, Ed., Polymer Data Handbook, Oxford University Press, New York, **1999**.

[22] B. Tian, G. Zerbi, *J. Chem. Phys.*, **1990,** *92(6),* 3886.

[23] B. Tian, G. Zerbi, *J. Chem. Phys.*, **1990,** *92(6),* 3892.

[24] T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds, Ed., Handbook of Conducting Polymers (2nd Edition), Marcel Dekker, New York, **1998**, p.409-421.

[25] G. B. Street, T. C. Clark, M. Krounbi, K. Kanazawa, V. Lee, P. Pfluger, J. C. Scott, G. Weiser, *Mol. Cryst. Liq. Cryst.*, **1982,** *83*, 253.

[26] T. C. Clark, J. C. Scott, G. B. Street, *IBM J. Res. Dev.*, **1983,** *27,* 313.

[27] C. Sawatari, and M. Matsuo, *Coll. & Polym. Sci.* **1985,** *263,* 783.

[28] M. Matsuo, C. Sawatari, and T. Ohhata, *Macromolecules* **1988,** *21*, 1317.

[29] M. Matsuo, M. Tsuji, R. St. J. Manley, *Macromolecules* **1983,** *16,* 1.