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The stability of polypyrrole and its composites

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The stability of chemically and electrochemically polymerized polypyrrole and its composites has been investigated. The results demonstrate that the oxidative degradation of polypyrrole and the interruption of the percolation path of the composites can cause a strong decrease in electrical conductivity. The possible mechanisms of oxidative degradation of polypyrrole and the interruption of the percolation path of the composites are also discussed.

1. Introduction

Electrically conductive organic polymers and their composites have been studied very intensively in the last few years. Much work in this area has been focused on polyacetylene and polypyrrole (PPY) [1]. The convenient electrochemical and chemical preparation of PPY affords a variety of anionically "doped" materials possessing a high electrical conductivity [2, 3]. A composite in which the PPY particle is embedded in an insulating polymeric matrix, can show an improvement in the poor mechanical properties [4]. Despite the enormous volume of scientific literature published on PPY and its composites, relatively few papers concentrate systematically on the stability of the electrical conductivity of PPY and its composites under different conditions. In fact, the stability of the electrical conductivity is very important for the industrial application of PPY and its composites.

We present here a study on the stability of chemically and electrochemically polymerized polypyrrole and its composites. The possible mechanisms of degradation are also discussed.

2. Experimental procedure

Chemically polymerized PPY was obtained by $FeCl_3$ chemical oxidative polymerization: $FeCl_3$ (98% pure, Merck) as oxidizing agent, pyrrole (GC, 99%, Aldrich) and acetonitrile (HLPC, 99.8%, Aldrich) were used. The polymerization procedure was as follows: $FeCl_3$ was firstly dissolved in distilled water (30% $FeCl_3$ aqueous solution), then a 10% pyrrole acetonitrile solution was added in drops into the 30% $FeCl_3$ aqueous solution which was continuously stirred during the polymerization process. The pyrrole/$FeCl_3$ molar ratio was 2/1. The PPY powder obtained by this way was washed first with distilled water then with acetonitrile.

The electropolymerization of PPY was based on the oxidation of pyrrole carried out in a three-electrode electrolytic cell in a solution of 0.10 M pyrrole and 0.10 M $LiClO_4$ (GC, 99.8%, Aldrich) dissolved in acetonitrile. A nickel plate was used as anode, with a platinum wire acting as a counter-electrode. A PPY film was subsequently obtained in this way.

The composites were prepared with low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polystyrene (PS) filled with chemically polymerized PPY particles. First PPY was added to the melted matrix and mixed for 5 min in a RAPRA micro-mixer. The mixture of LDPE/PPY, HDPE/PPY and PS/PPY was then pressed into a plate by compression moulding at 120 °C for PE/PPY and 150 °C for PS/PPY under a pressure of 20 MPa for 5 min, and then for 10 min under the same pressure at room temperature.

In order to measure the electrical conductivity, the PPY powder was compacted under pressure in order to obtain a thin pellet. The typical sample dimensions were 3 mm × 15 mm with a thickness of 0.2–0.4 mm. The electrical conductivity was measured using a four-probe technique [5] for the chemically polymerized PPY and by Van der Pauw method [6] for the electrochemically polymerized PPY. The electrical conductivity of the composite sample with dimensions 2 mm × 5 mm × 30 mm was measured by means of a Keithley 617 programmable electrometer. The sample contact surfaces to the probes were polished by means of sand paper and a silver paint was used in order to decrease the contact resistance.

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3. Results and discussion

Fig. 1 shows the variation of the electrical conductivity of PPY versus time in air at 20 ± 2 °C. A decrease of electrical conductivity with time is observed. For the chemically polymerized PPY, the decrease of electrical conductivity is more important than for the electrochemically polymerized PPY.

Two mechanisms may explain the difference in the observed decrease of the electrical conductivity of PPY. On the one hand, the chemically and electrochemically polymerized PPY are doped by Cl^- and ClO_4^-, respectively. At a high doping level, the Cl^- may be fixed into the PPY chain [7]. This leads to the destruction of the π electron system of PPY with the formation of the covalent carbon-chlorine bond which could act as electron traps. On the other hand, because the chemically and electrochemically polymerized polypyrroles are a powder with a diameter of ~0.5 μm and film, respectively, as shown in Fig. 2, the chemically polymerized PPY samples prepared with compacted PPY powder have a much larger specific surface than the electrochemically polymerized PPY film. An oxidative mechanism can take place which should be more active on chemically polymerized PPY owing to its large specific surface. This oxidized surface phase surrounding the PPY particles could be responsible for the considerable decrease in electrical conductivity of the sample. This is due to the fact that the electrical conductivity of the superficially oxidized PPY phase is much lower than that of the core of the PPY particle thus increasing the contact resistance between PPY particles.

The variations in electrical conductivity of chemically polymerized PPY at different temperatures are shown in Fig. 3. At high temperature, the electrical conductivity decreases very quickly when PPY is exposed to the air. However, under an argon atmosphere, the electrical conductivity is stable even at 200 °C (Fig. 3b). We can, therefore, consider that the decrease of the electrical conductivity of PPY at high temperature results from a chemically oxidative degradation. In the absence of oxygen, PPY is thermostable.

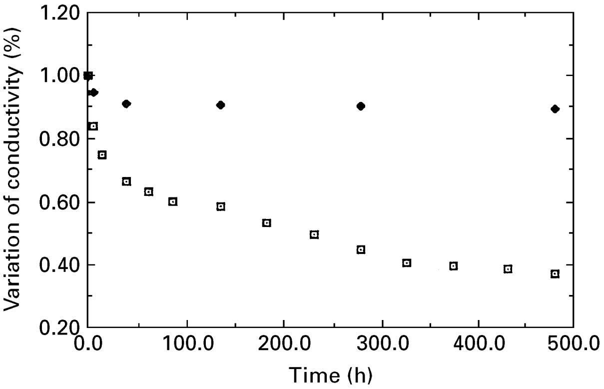

Figure 1 Variation of electrical conductivity of chemically and electrochemically polymerized polypyrrole in air at 20 ± 2 °C. (□) chemically polymerized polypyrrole, (◆) electrochemically polymerized polypyrrole.

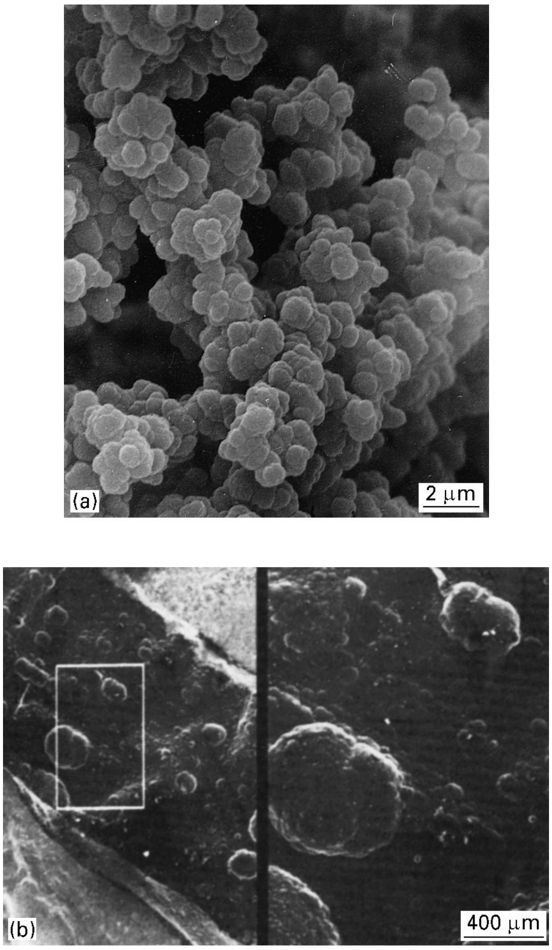

Figure 2 Micrographs of polypyrroles: (a) chemically polymerized polypyrrole, (b) electrochemically polymerized polypyrrole.

If the decrease of electrical conductivity of PPY is used as a measure of the degradation rate, the chemically oxidative degradation can be expressed by a first-order kinetics within a certain temperature range

$$\log(\sigma_t/\sigma_0) = Kt \qquad (1)$$

σ_t and σ_0 are electrical conductivities at the time t and at the beginning of the reaction, respectively, and K is the degradation constant. The different values of the constant K at different temperatures are reported in Table I. A linear relationship between the logarithm of that degradation constant and the inverse of temperature is found. Therefore, we can use Arrhenius' formula to obtain the activation energy of the oxidative reaction

$$K = Ae^{-E/RT} \qquad (2)$$

where E is the activation energy of the reaction, R the gas constant and T the temperature. The value of the activation energy of the degradation is about 11 kcal mol^{-1}, which is close to the activation energy for the formation of the carbonyl group in polyacetylene [7].

The stability of the composites filled with PPY in time with respect to electrical conductivity has also been investigated. The results are shown in Fig. 4. We found that the electrical conductivity of the composites is almost constant at room temperature. However, when the LDPE/PPY composite is annealed at 55 or 80 °C, its electrical conductivity decreases first rapidly with increase of annealing time. The decrease

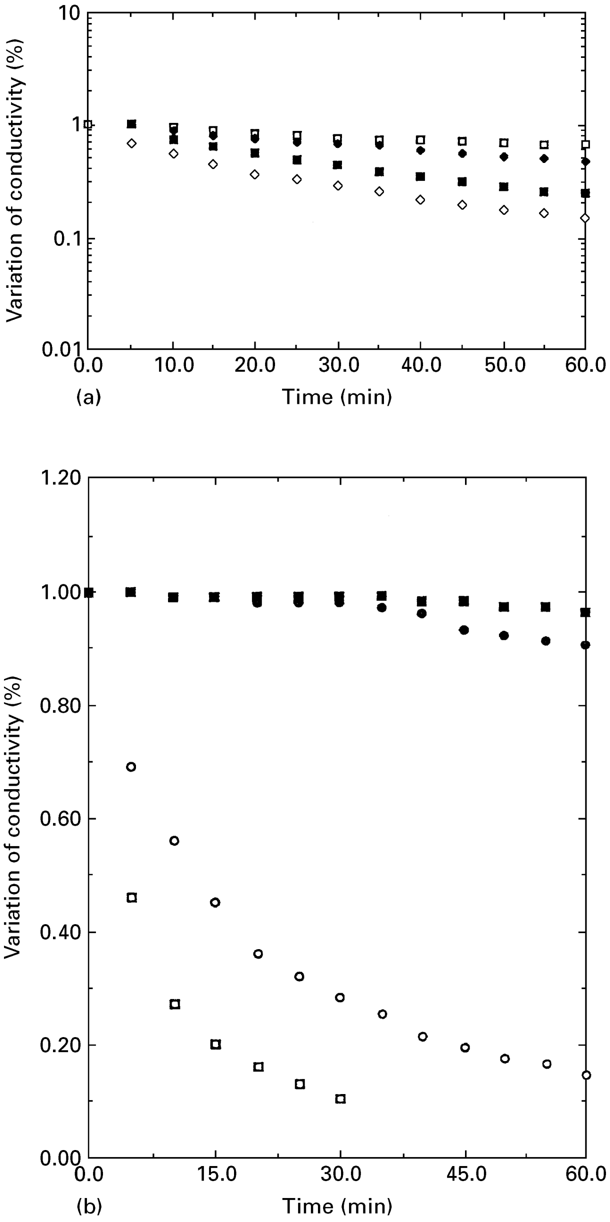

Figure 3 Electrical conductivity of chemically polymerized polypyrrole as a function of time under different conditions: (a) in air, at (□) 120 °C, (◆) 135 °C, (■) 150 °C, (◇) 165 °C; (b) (○, □) in air; (●, ■) under argon at (○) 165 °C, (□, ■) 180 °C, (●) 200 °C.

TABLE I Degradation constants of polypyrrole in air

Temperature (K)	Degradation constant $(10^{-4}\mathrm{s}^{-1})$
453	4.16
438	2.04
423	1.85
408	1.02
393	0.61

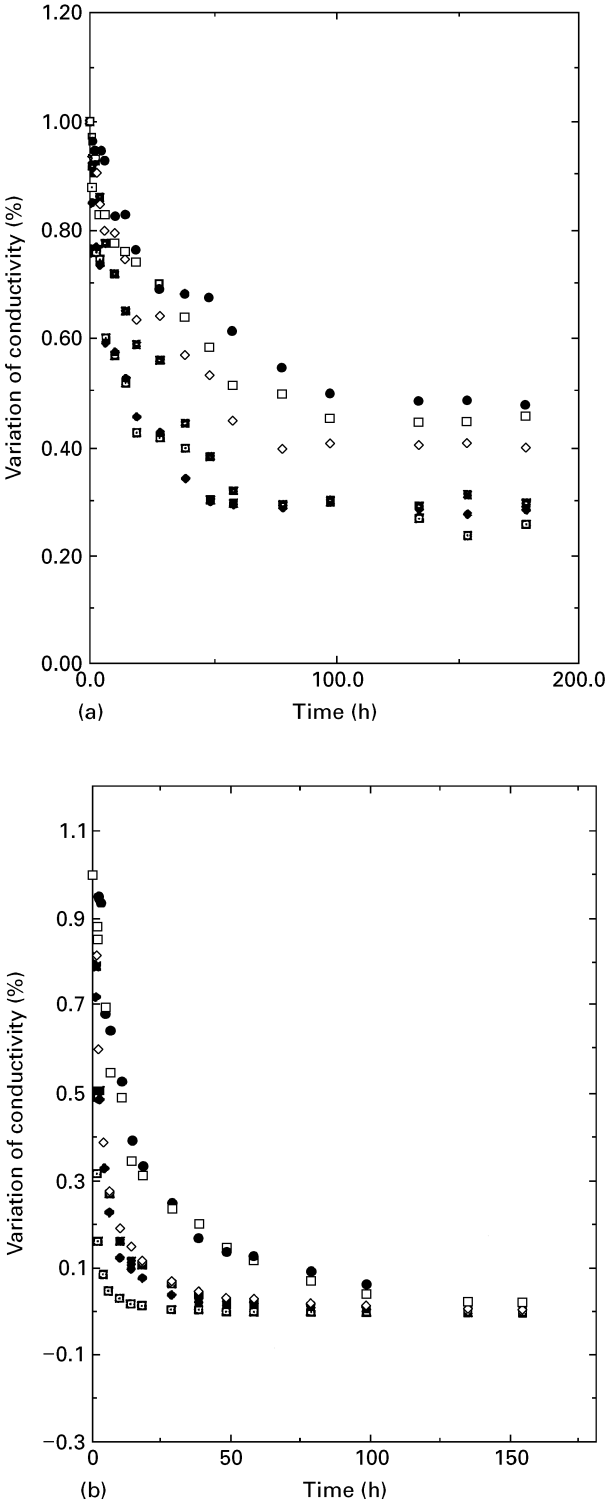

Figure 4 Electrical conductivity of LDPE/PPY composites as a function of time at different temperatures: (a) 55 °C (⊡) 15%, (◆) 20%, (■) 25%, (◇) 30%, (●) 35%, (□) 40%; (b) 80 °C (⊡) 10%, (◆) 15%, (■) 20%, (◇) 25%, (●) 35%, (□) 40%.

of electrical conductivity is faster for LDPE/15 wt% PPY composite than for LDPE/30 wt% PPY composite. These results suggests that the decrease of electrical conductivity of the composites does not result from the decrease in electrical conductivity of PPY.

Fig. 5 shows the influences of different matrices on the electrical conductivity of composites. It was found that the thermo-mechanical stability of matrices is PS > HDPE > LDPE and the stability of the electrical conductivity of composites is PS/PPY > HDPE/PPY > LDPE/PPY.

The electrical conductivity of the composite filled with PPY particles depends on the percolation path, which consists of PPY particles in direct contact or separated by very small distances. In the latter case,

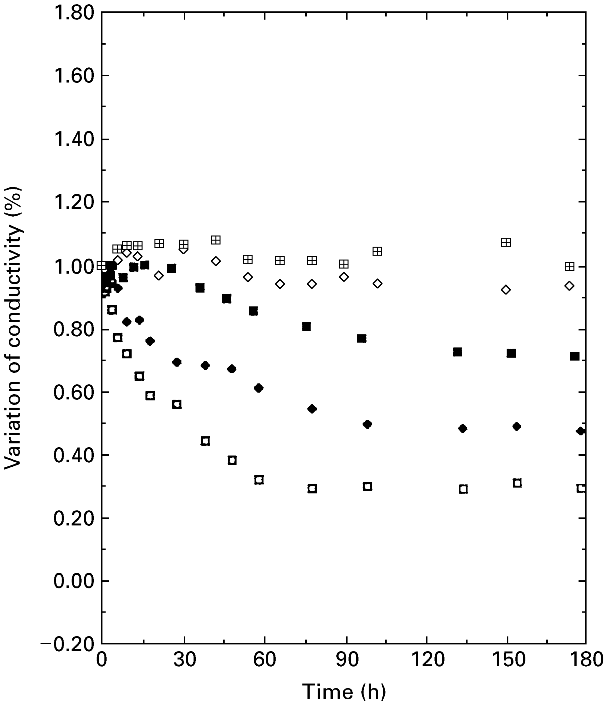

Figure 5 Influence of different polymer matrices on the stability of the electrical conductivity of composites at 55 °C. PE(B): LDPE; PE(M): HDPE; PS: PS, (□) PE(B) + 25% PPY; (◆) PE(B) + 35% PPY; (■) PE(M) + 20% PPY; (◇) PS + 25% PPY, (■) PS + 35% PPY.

the current passes from one particle to another by tunnelling [8]. The decrease in electrical conductivity of the composite is related to the interruption of the percolation path. Because of the variation in the specific volume of non-crystalline polymers before and after their T_g, while the annealing temperatures (55, 80°C) are higher than the T_g of polyethylene, and lower than the T_g of PPY, the thermal expansion of polyethylene and PPY is different at the annealing temperature. When the composite is annealed, the distance between the PPY particles first increases because of the different thermal expansion between the matrix and the charge. Then, if at this temperature a relaxation of the polymer matrix chain occurs, it may change the contact situation between PPY particles and result in either an interruption of the direct contact or an increase of the distance between the PPY particles, thus leading to the variation in structure of composite. In this case, when the composite is rapidly recooled to room temperature, the variation in structure will remain and the electrical conductivity of composite decreases.

The polymer chain relaxation depends on the thermo-mechanical stability of the polymer. The higher the thermo-mechanical stability of the polymer, the longer is time needed for the chain relaxation of the polymer. If the relaxation time of the matrix is longer than the annealing time, the chain relaxation of the matrix cannot occur during annealing. Thus when the composite is recooled to room temperature, variation of the structure of the composite caused by the different thermal expansions of the matrix and the charge, will disappear and the electrical conductivity of the composite is stable. The T_g of PS is about 110 °C, when the PS/PPY composite is annealed at 55 °C, the chain relaxation cannot occur under this annealing condition, and thus we can observe that the electrical conductivity of PS/PPY composite is stable during annealing.

4. Conclusion

The decrease in electrical conductivity of PPY seems to be mainly caused by a chemically oxidative degradation at high temperature, which follows a first-order reaction. The oxidative degradation is more active for chemically polymerized PPY owing to the larger specific surface of the PPY particles.

The decrease in electrical conductivity of the composite is attributed to the interruption of the percolation path, which is related to the thermal expansion of the composite and the relaxation of the polymer matrix chain. The thermo-mechancial stability of the matrix influences the chain relaxation and thus the stability of the electrical conductivity of the composites.

References

1. B. SCROSATI *Prog. Solid. State. Chem*, **18** (1988) 1.
2. Y. E. WHANG, H. TAKINO, J. H. HAN *et al.* ICSM'90 (1990).
3. B. F. CRETKO, M. P. BRUNGS, *et al. J. Mater. Sci* **23** (1988) 2102.
4. B. WESSLINF and H. VOLK, *Kunststoffe* **76** (1986) 930.
5. A. K. SIRCAR and J. L. WELLS, *Polym. Eng. Sci* **21** (1981) 809.
6. L. J. VAN DER PAUW, *Philips Res. Rep.* **13** (1958) 1.
7. M. A. HALEEM, PhD thesis, Universite de Nancy I (1989).
8. E. VALOT, PhD thesis, Universite Bordeaux I (1990).

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