Korean J. Chem. Eng., **28**(2), 440-444 (2011)
DOI: 10.1007/s11814-010-0374-5

Synthesis of copper-poly tetrafluoro-ethylene composites by supercritical impregnation process

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(*Received 10 June 2010 • accepted 12 July 2010*)

Abstract−This study attempted to develop a copper-PTFE composite consisting of copper nano-particles homogeneously distributed into PTFE using $scCO_2$. The overall synthesis process consisted of impregnation of copper precursor and thermolytic reduction. The impregnation process was performed over a range of temperature from 40 to 160 °C and pressure from 120 to 200 bar. The reduction process was performed at 230 °C and 250 bar for 2 hours consecutively after impregnation. The changes in appearance, mass, and morphology of the PTFE composite were examined by precision balance, SEM, TEM, and EDS. The impregnation ratio increased with temperature up to 120 °C, but decreased above 120 °C. The impregnation ratio increased with the pressure. These results could be explained by dehydration reaction of $Cu(hfa)_2H_2O$ and thermodynamical affinity difference of copper precursors for PTFE or $scCO_2$. Copper nano-particles impregnated into the PTFE were identified from SEM, TEM and EDS analysis.

Key words: Supercritical, Impregnation, PTFE, Copper Bis(Trifluoroacetylacetonate), Nano-particle

INTRODUCTION

$ScCO_2$ (supercritical carbon dioxide) has unique mass transport properties, which are engaged in extraction and impregnation applications [1]. Berens et al. [2] suggested that compressed CO_2 could be useful to facilitate the impregnation of additives into glassy polymers. The important role of CO_2 is its plasticizing effect on polymers during penetration. The plasticization is caused by the sorption of high amounts of a penetrant that interacts strongly with the polymer; the glassy polymer can thus transform from the glassy state to a rubbery. In a rubbery state, the polymer chains can move more freely, which makes polymer impregnation with additives more efficient [3-6]. That is, polymers are swollen by $scCO_2$ so that they may be impregnated rapidly with additives.

Because of this property, supercritical impregnation is explored for the formulation of drug-delivery devices [7,8], for the dyeing of hard-to-dye fibers in the textile industry [9], for the deposition of nanofillers into substrates [10], to create new polymeric blends through infusion of a monomer and subsequent polymerization, or as a first step of the devulcanization process of rubber [4].

Metallopolymer nanocomposites exhibit some unusual structural, magnetic, catalytic and biological properties untypical for large particles, owing to their small size [11]. An original method using supercritical fluids, especially $scCO_2$, for the metallopolymer nanocomposite synthesis was proposed by Watkins and McCarthy [12]. The method is performed in two steps. The first step,called the supercritical infusion process or supercritical impregnation process [2], is the diffusion of organometallic precursors dissolved in $scCO_2$ into polymer matrix. The second step is the reduction process of the precursor to the metal. The method using $scCO_2$ can induce metal nanoparticles homogeneously distributed throughout polymer matrix.

Generally, metal complexes that contain fluoroacetylacetonate or cyclooctadecyl ligands have relatively high solubility in $scCO_2$, but the impregnation ratio of impregnants into the polymers is not proportional to solute concentrations in $scCO_2$ [1-4,13]. Nevertheless, these metal complexes have been used to fabricate metallopolymer composites by supercritical impregnation [9,12].

The aim of this study is to develop the copper-PTFE composite consisting of copper nano-particles homogeneously distributed into PTFE (poly tetrafluoroethylene) using $scCO_2$ as a carrier for the tribological application. In this study, we adapted $Cu(hfa)_2H_2O$ (Copper bis(trifluoroacetylacetonate) hydrate) and PTFE as copper precursor and polymer matrix, respectively.

EXPERIMENTAL

1. Equipment and Procedures

The schematic experimental apparatus for the copper-PTFE composite synthesis using $scCO_2$ is depicted in Fig. 1. The apparatus consisted of a low-temperature bath, high pressure pump, two consecutive high pressure cylinders and auxiliary facilities. A borescope (Rigid Borescope, Olympus®) was installed on the 'Cylinder 2' to observe the inside of the cylinder.

$Cu(hfa)_2H_2O$, copper precursor, was purchased from TCI with a purity of 95%. PTFE sheet and film whose thickness is 1 mm and 0.1 mm were provided from Jinil Tec-Pla. Co., Ltd. (Korea), and experimental specimens had dimension of 1×10×100 mm and 0.1×10×100 mm. The experiments were carried out as described below.

$Cu(hfa)_2H_2O$ and PTFE were loaded in the 'Cylinder 2', and the system was purged with pure CO_2 for 10 minutes to eliminate air inside cylinders. 'Cylinder 2' was heated to a desired temperature. Liquid CO_2 was then pumped into the cylinders to achieve the desired pressure. 'Cylinder 1' was used in order to relieve the shock

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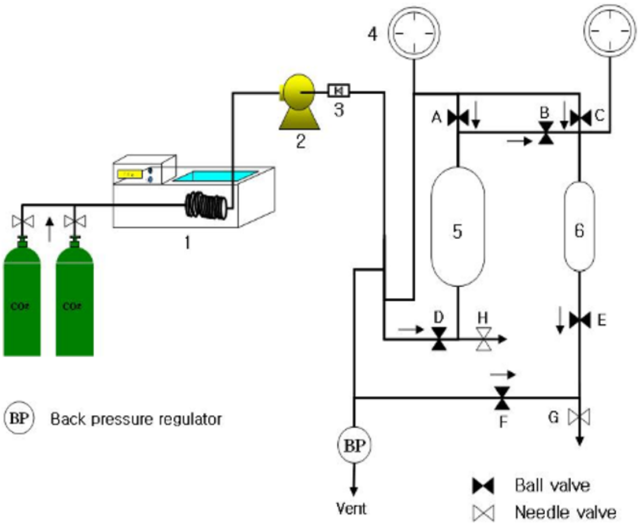

Fig. 1. Schematic diagram of supercritical equipment for the copper-PTFE composite synthesis.

1. Low temperature bath	4. Pressure gauge
2. Pump	5. Cylinder 1 (100 mL)
3. Check valve	6. Cylinder 2 (50 mL)

of pressure fluctuation that occurred when CO_2 was pumped into the ‘Cylinder 2’. For the proper operation, CO_2 was supplied to the top of ‘Cylinder 2’ via the bottom of ‘Cylinder 1’. After ‘Cylinder 2’ was pressurized, the CO_2 flow was disconnected. And ‘Cylinder 2’ was maintained for the duration in order to impregnate PTFE with copper precursors.

The experimental scope of temperature and pressure was 40-160 °C and 120-200 bar. The impregnation was maintained for 20 hours in order to examine the effect of temperature and pressure.

When the impregnation process was completed, we performed the thermolytic reduction prior to decompression in order to reduce copper precursors to copper. All thermolytic reductions were induced by raising the temperature of ‘Cylinder 2’ to 230 °C [16] and were carried out for 2 hours at 250 bar. Then ‘Cylinder 2’ was depressurized and washed with pure CO_2 for 10 minutes at 60 bar and copper-PTFE composites were collected from the ‘Cylinder 2’.

2. Characterization

The changes in appearance, mass, and morphology of the copper-PTFE composites were examined by precision balance (Sartorius BP210S, resolution 10^{-4} g), scanning electron microscopy (SEM, JSM-6700F, Jeol), transmission electron microscopy (TEM, H-7500, Hitachi) and energy-dispersive X-ray spectroscopy (EDS).

To determine the amount of copper precursors impregnated into PTFE, the mass gain of the impregnated PTFE samples was measured by precision balance. To study cross-sectional morphology of synthesized copper-PTFE composites, SEM and TEM analysis was applied. For the preparation of TEM samples, copper-PTFE composites with 0.1 mm thickness were sliced to 140 nm by cryomicrotome at −140 °C.

RESULTS AND DISCUSSION

For the synthesis of the copper-PTFE composite, experiments proceeded in two steps. The first step was supercritical impregnation of copper precursor and the effects of temperature and pressure on impregnation of copper precursor into PTFE were examined. The second step was the thermolytic reduction process performed at a $scCO_2$ atmosphere. The thermolytic reduction was followed by the impregnation process without decompression.

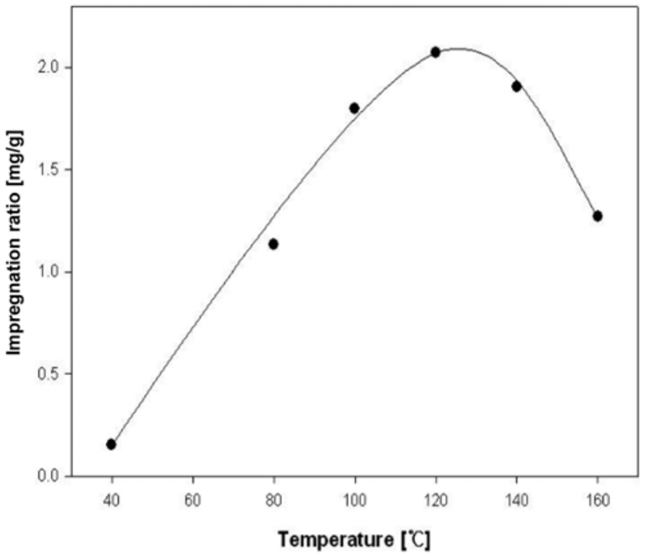

Fig. 2. Effect of temperature on the impregnation of copper precursor into PTFE at 160 bar.

1. Supercritical Impregnation Process

The effect of temperatures for the supercritical impregnation process was examined and the result is shown in Fig. 2. It was confirmed that the impregnation ratio increased with temperature up to 120 °C and then decreased with temperature. This result might be due to the chemical change of copper precursor, $Cu(hfa)_2H_2O$, and affinity of impregnant between $scCO_2$ and polymer. From the borescopic observation into ‘Cylinder 2’, it was identified that the color of the supercritical solution was blue at low temperature and turned to orange at 160 °C. Their images are shown in Fig. 3. The impregnated samples showed the same color with the supercritical solution at each temperature.

Garriga et al. [15] reported that a purple color appeared due to dehydration of $Cu(hfa)_2H_2O$ as the temperature of the reactor increased to 200 °C in supercritical media. In this study, however, the color of the supercritical solution observed by the borescope at 160 °C was orange, and this orange color is guessed to be connected with dehydration equilibrium between $Cu(hfa)_2$ and $Cu(hfa)_2H_2O$.

It is also well known that the impregnation ratio depends on the relative affinity of impregnant between $scCO_2$ and the polymers for the supercritical impregnation process [1-4,13,16,17]. The $scCO_2$ impregnation process actually involves the approach toward an equilibrium distribution of five components [PTFE, CO_2, $Cu(hfa)_2H_2O$, $Cu(hfa)_2$, H_2O] between the phases present. However, phase relations for a five-component system are very complex. Therefore, a somewhat simplified approach seems appropriate for the discussion on the effect of temperature. Lagalante et al. [18] measured the solubility of $Cu(hfa)_2$ and $Cu(hfa)_2H_2O$ in $scCO_2$ and showed that $Cu(hfa)_2$ dissolved more than $Cu(hfa)_2H_2O$ in $scCO_2$. Therefore, it seems to be valid that $Cu(hfa)_2$ has more affinity than $Cu(hfa)_2H_2O$

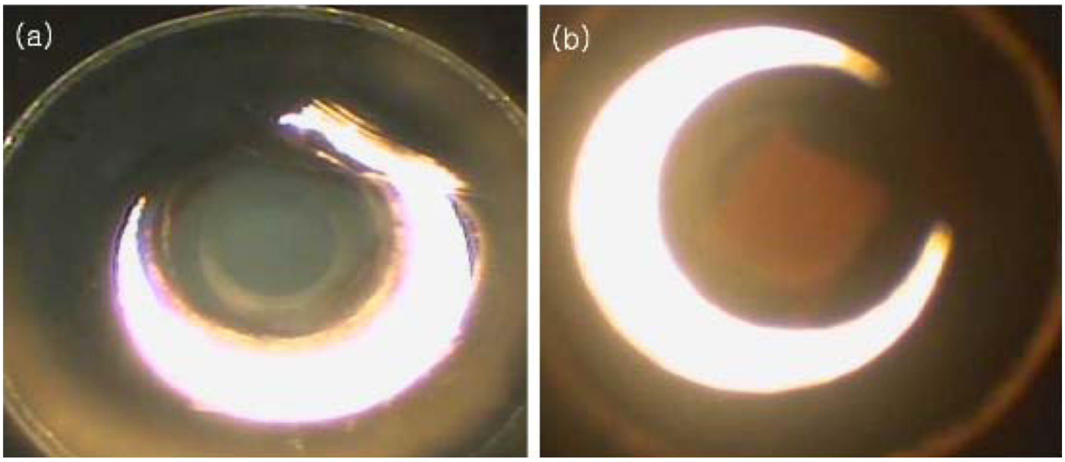

Fig. 3. PTFE samples in copper precursor supercritical solution observed by borescope at 160 bar; (a) 80 °C (b) 160 °C.

for $scCO_2$.

For the effect of temperature, we could explain that the increase in impregnation ratio up to 120 °C might be attributable to affinity of $Cu(hfa)_2H_2O$ for PTFE, and the decrease in impregnation ratio above 120 °C might be to occur because $Cu(hfa)_2$ produced by dehydration of $Cu(hfa)_2H_2O$ has more affinity for $scCO_2$.

The relation between the impregnation ratio and pressure is shown in Fig. 4. The impregnation ratio increased with pressures, but the ratio shows almost similar values above 160 bar.

Berens et al. [2] reported that the diffusivity of impregnant increased with pressure, but the equilibrium impregnation ratio decreased with pressure for the supercritical ternary system (polyvinyl chloride, dimethyl phthalate, and CO_2). They mentioned that the major effect of CO_2 is accelerating the kinetics of additive absorption when the interaction between a polymer and an additive is favored thermodynamically.

For the $scCO_2$ solution, it is well known that the solubility of a solute increases with pressure because the increase in pressure improves the affinity of a solute for $scCO_2$. That means the relative affinity for PTFE decreases with pressure. Therefore, for pressure up to 160 bar, diffusivity of $Cu(hfa)_2H_2O$ in PTFE seems to affect more than the affinity for PTFE. However, for the pressure over than 160 bar, the diffusivity of $Cu(hfa)_2H_2O$ may be considered to have the similar effect on the impregnation process with the affinity for PTFE and $scCO_2$.

From these results of temperature and pressure effect, we could determine that the optimum process condition from the viewpoint of diffusivity and affinity for PTFE was 120 °C and 160 bar.

Experimental researches on the impregnation equilibrium time at the optimum process condition were performed and the results are shown in Fig. 5. From the Fig. 5, it turns out that the impregnation equilibrium time is about 55 hours at 120 °C and 160 bar.

2. Thermolytic Reduction Process

PTFE samples impregnated at 120 °C and 160 bar were supercritically reduced at 230 °C and 250 bar for the preparation of copper-PTFE composites. This reduction process was based on Garriga's result.

Garriga et al. [15] reported that copper appeared above 190 °C

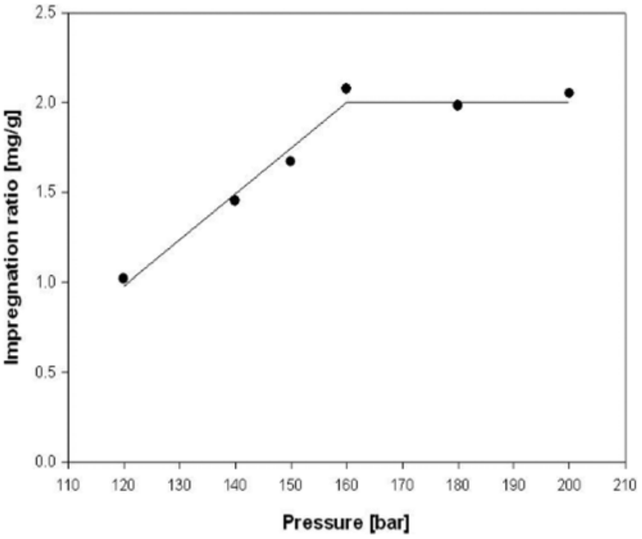

Fig. 4. Effect of pressure on the impregnation of copper precursor into PTFE at 120 °C.

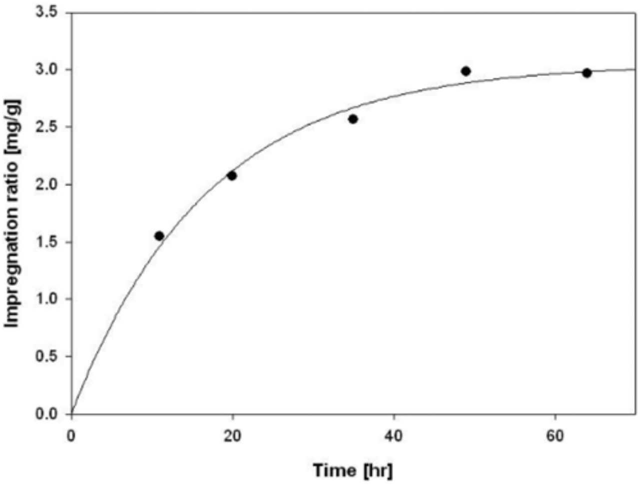

Fig. 5. Time profile of the impregnation process for copper precursor into PTFE at 120 °C, 160 bar.

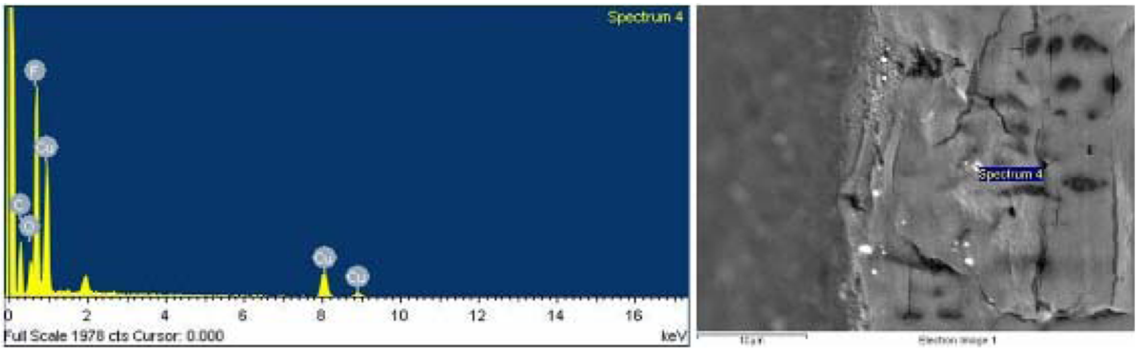

Fig. 6. EDS analysis on the cross section of the copper-PTFE composite synthesized using scCO$_2$; impregnation at 120 °C, 160 bar/reduction at 230 °C, 250 bar.

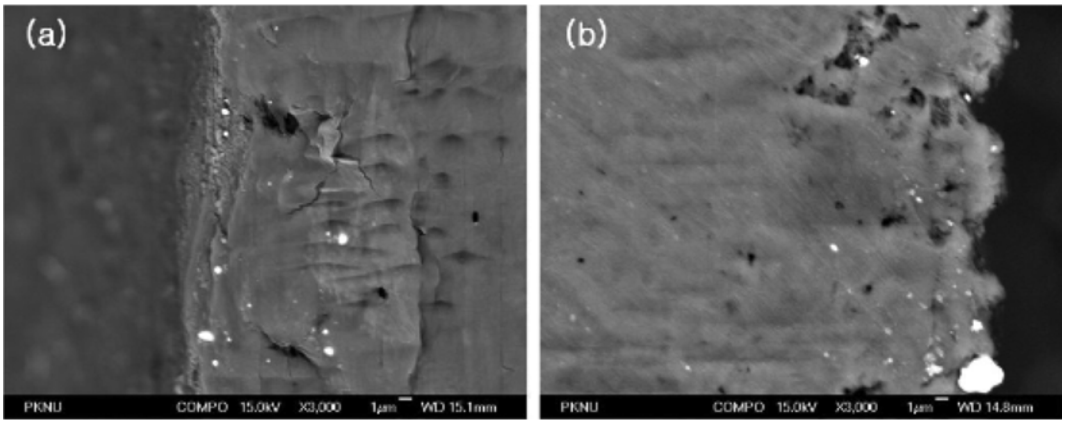

Fig. 7. Cross sectional SEM images of the copper-PTFE composite synthesized using scCO$_2$; (a) impregnation at 120 °C, 160 bar (b) impregnation at 120 °C, 180 bar/reduction at 230 °C, 250 bar.

when Cu(hfa)$_2$H$_2$O was pyrolyzed in supercritical condition of CO$_2$-ethanol mixture of molar composition 80 : 20%. And they reported that the solubilities of Cu(hfa)$_2$H$_2$O and Cu(hfa)$_2$ in scCO$_2$ were increased and the precursor decomposition temperature was about 30 °C lower than in pure CO$_2$ when ethanol was added as co-solvent. Therefore, we adopted 230 °C as the reduction temperature.

The existence of copper in the resultant composites was confirmed by EDS and SEM analysis on the cross-section. EDS analysis and SEM images on the cross section of the composites are shown in Fig. 6 and Fig. 7. From Fig. 6, we could identify that white spots inside the synthesized composite are copper particles.

Fig. 7 shows that copper particles are more deeply penetrated in the copper-PTFE composite synthesized at 180 bar than in the composite synthesized at 160 bar. If the composite reached at impregnation equilibrium, copper would be homogeneously dispersed in all regions of the cross-section. Therefore Fig. 7 indicates that the

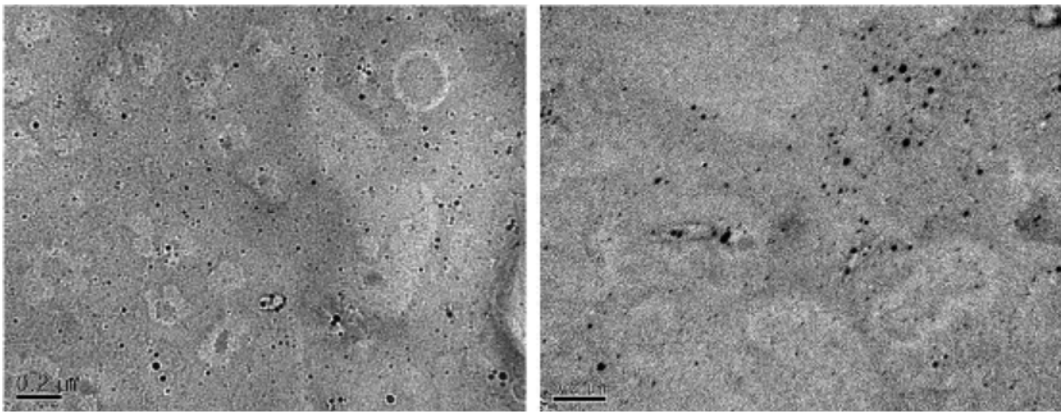

Fig. 8. Cross sectional TEM images of the copper-PTFE composite synthesized using scCO$_2$; impregnation at 120 °C, 160 bar/reduction at 230 °C, 250 bar.

composite did not reach impregnation equilibrium yet. From this result, we could identify that diffusivity increases with pressure as mentioned in the literature [2].

Finally, we attempted to synthesize a copper-PTFE composite in which copper particles were dispersed homogeneously. An experiment using a PTFE film with 0.1 mm thickness was carried out in order to shorten the impregnation equilibrium time. Impregnation and reduction were consecutively performed at 120 °C, 160 bar for 2 hours and at 230 °C, 250 bar for 2 hours. Its TEM images are shown in Fig. 8. From images, we learned that copper particles were dispersed homogeneously inside the synthesized composite and impregnation equilibrium had been reached. The size of copper particles was less than 20 nm.

CONCLUSIONS

Experimental researches have been made for the development of copper-PTFE composite consisting of copper nano-particles homogeneously distributed into PTFE using $scCO_2$ and some valuable results were obtained.

The impregnation ratio of copper precursor increased with temperature up to 120 °C, but decreased above 120 °C. The impregnation ratio increased with pressure up to 160 bar and showed similar values for the pressure over than 160 bar. It seems to be caused by the dehydration reaction of $Cu(hfa)_2H_2O$ and thermodynamic affinity difference of copper precursors for PTFE and $scCO_2$.

From the effects of temperature and pressure on the impregnation, we could obtain that the optimum impregnation process condition was 120 °C and 160 bar.

PTFE supercritically impregnated with the copper precursor at 120 °C and 160 bar was effectively reduced at 230 °C and 250 bar to prepare copper-PTFE composites.

SEM images and EDS analysis indicated that copper particles were penetrated into the synthesized composites. Finally, from TEM images, we could identify that copper-PTFE composites with homogeneously dispersed copper particles could be made.

REFERENCES

1. O. Muth, Th. Hirth and H. Vogel, *J. Supercrit. Fluids*, **17**, 65 (2000).
2. A. R. Berens, G. S. Huvard, R. W. Korsmeyer and F. W. Kunig, *J. Appl. Polym. Sci.*, **46**, 231 (1992).
3. S. Diankov, D. Barth, A. Vega-Gonzalez, I. Pentchev and P. Subra-Paternault, *J. Supercrit. Fluids*, **41**, 164 (2007).
4. M. Kojima, S. Kohjiya and Y. Ikeda, *Polymer*, **45**, 2016 (2005).
5. J. Crank, The Mathematics of Diffusion, Clarendon Press, Oxford (1975).
6. P. Neogi, in Diffusion in Polymers, P. Neogi, Ed., Marcel Dekker, Inc., New York, 173 (1996).
7. C. Elvira, A. Fanovich, M. Fernández, J. Fraile, J. S. Ramán and C. Domingo, *J. Controlled Release*, **99**, 231 (2004).
8. S. Üzer, U. Akman and Ö. Hortaçsu, *J. Supercrit. Fluids*, **38**, 119 (2006).
9. S. Yoda, Y. Takebayashi, T. Sugeta and K. Otake, *J. Non-Cryst. Solids*, **350**, 320 (2004).
10. V. N. Bagratashvili, L. D. Bogomolova, V. I. Gerasimova, V. A. Jachkin, N. A. Krasil'nikova, A. O. Rybaltovskii and S. I. Tsypina, *J. Non-Cryst. Solids*, **345 & 346**, 256 (2004).
11. E. Said-Galiyev, L. Nikitin, R. Vinokur, M. Gallyamov, M. Kurykin, O. Petrova, B. Lokshin, I. Volkov, A. Khokhlov and K. Schaumburg, *Ind. Eng. Chem. Res.*, **39**, 4891 (2000).
12. J. J. Watkins and T. J. McCarthy, *Chem. Mater.*, **7**, 1991 (1995).
13. J. von Schnitzler and R. Eggers, *J. Supercrit. Fluids*, **16**, 81 (1991).
14. V. K. Popov, V. N. Bagratashvili, A. P. Krasnov, E. E. Said-Galiyev, L. N. Niktin, O. V. Afonicheva and A. D. Aliev, *Tribology Lett.*, **5**, 297 (1998).
15. R. Garriga, V. Pessey, F. Weill, B. Chevalier, J. Etourneau and F. Cansell, *J. Supercrit. Fluids*, **20**, 55 (2001).
16. T. T. Ngo, C. L. Liotta, C. A. Eckert and S. G. Kazarian, *J. Supercrit. Fluids*, **27**, 215 (2003).
17. J. Gregorowicz, *Fluid Phase Equilib.*, **238**, 142 (2005).
18. A. F. Lagalante, B. N. Hansen and T. J. Bruno, *Inorg. Chem.*, **34**, 5781 (1995).
19. B. Wong, S. Yoda and S. M. Howdle, *J. Supercrit. Fluids*, **42**, 282 (2007).