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SURFACE MODIFICATION OF CLAY PARTICLES WITH POLYANILINE SHELLS BY ANILINE POLYMERIZATION IN THE PARTICLES PRESENCE

Narkis Moshe*[1], Segal Ester [1], Jia Wentao [1], Siegmann Arnon[2]

Department of Chemical Engineering[1]
Department of Materials Engineering[2]
Technion – IIT, Haifa 32000, Israel

Recently, catalytic polymerization on solid surfaces has become an attractive method for the production of polymer/filler composites. The concept of polymerizing a monomer in the presence of particles of catalyzed surfaces can be widely employed to encapsulate inorganic or organic particles with conducting or insulating polymers[1]. This approach was employed for the synthesis of unique polyaniline (PANI)/clay composites and nanocomposites [2-4].

In this process anilinium-DBSA complex, the monomer, is polymerized to PANI-DBSA (DBSA, dodecyl benzene sulfonic acid, being the dopant) as an aqueous dispersion in the presence of particles of mica or talc clays. It was found that the clay presence greatly accelerates the polymerization process by reduction of the typical long induction[5] (reduction of ~1 order of magnitude) and also by reduction of the total polymerization time. The chemical composition of mica and talc, contains some metallic cations, besides silicon and oxygen, e.g., Fe^{+3}/Fe^{+2}, Mg^{+2}, Ca^{+2}, Al^{+3}, etc. To investigate their catalytic effect, small quantities of several metallic salts were added to the anilium-DBSA polymerization reaction. It was found that Fe^{+2}/ Fe^{+3} ions, present in the clays' structures, are responsible for the acceleration in the polymerization kinetics of anilinium-DBSA (the catalytic effect of Mg^{+2}, Ca^{+2} and Al^{+3} ions on the polymerization kinetics was very small). Moreover, the aniline preferentially polymerizes upon the clay particles' surface, thus, causing their encapsulation by fine PANI-DBSA shells. Further coating with PANI-DBSA takes place on the already coated particles with thin PANI-DBSA shells by an autoacceleration effect of anilinium-DBSA polymerization by the PANI-DBSA.

The catalytic/autoacceleration effect dominating in this process was extended for the synthesis of PANI-DBSA/organophilic-clay nanocomposites (organically modified montmonrillonite clay) by an in-situ intercalation/polymerization method[4]. Trends of the polymerization process are similar to those of the PANI-DBSA/mica composites. It was found that the montmonrillonite clay also has a catalytic effect on the polymerization of anilinium-DBSA. However, in addition to engulfment, intercalation of anilinium-DBSA into the galleries occurs as well. The intercalation into the galleries of the organo-clay was confirmed by X-ray diffraction analysis and significantly large d-spacing expansions from, 13.3Å to 29.6Å, for the nanocomposites prepared at different conditions were observed. For comparison, a PANI-DBSA/untreated montmonrillonite composite was also studied. X-ray results for the latter indicate that no intercalation has taken place. Thermogravimetric analysis demonstrated enhancement of the thermal stability in air of the nanocomposites relative to the bulk polymers.

References

1. Wypych, G.; Handbook of Fillers, ChemTec Publishing, 2nd Edition, Canada (1999).
2. Segal, E.; Aviel, O.; Narkis, M. Polym. Eng. Sci. 2000, 40, 1915.
3. Jia, W.; Segal, E.; Narkis, M.; Siegmann, A. Polym. Adv. Tech. 2002, 13, 16.
4. Jia, W.; Segal, E.; Narkis, M.; Siegmann, A. Synth. Metals, 2002, 128, 115.
5. Haba, Y.; Segal, E.; Narkis, M.; Tietelman, G.I; Siegmann, A. Synth. Metals, 1999, 106, 59.