*Materials Science, Vol. 21, No. 4, 2003*

# Synthesis of nanosilica by the sol-gel method and its activity toward polymers

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Applicability of the sol-gel method to fabricate polymer-silica composites has been briefly reviewed. The sol-gel method has been applied for synthesis of nanosilica in mineral and naphthenic oils and also in latexes of diene copolymers. A new silane precursor of nanosilica was prepared by transesterification of tetraethoxysilane with *n*-decyl alcohol and (aminopropyl)trimethoxysilane, in the presence of an emulsifier and a stabilizer. Transparent sols of nanosilica in oils were obtained as the main product, accompanied by few % of dispersions of $SiO_2$. Microscope and AFM studies confirmed the presence of particles of nanometric size. The studies are continued in order to optimize reaction conditions and minimize the size of $SiO_2$ particles. Nanosilica sols are applied for modification of properties of elastomers and other polymers. New hybrid modifiers of general formula $X(Me_2SiO)_4R$ have been prepared. Their chemical structures were confirmed by spectroscopic methods: FT-IR and NMR ($^1H$, $^{29}Si$-). These new products have been applied for synthesis of modified silica nanoparticles in elastomers matrices (*in situ*).

Key words: *sol-gel; nanosilica; modification of polymers*

## 1. Introduction

A quickly growing range of applications of nanomaterials in many fields has been observed in recent years [1, 2], nanosilica being often used in these studies [3]. Graft polymerization of vinyl monomers onto nanoalumina was accomplished through the free radical polymerization with the participation of double bonds at the particle surfaces, preintroduced by a silane coupling agent modification of the alumina [4]. An advantageous effect of nanoparticles on the properties of nanocomposites has been presented in the literature [5].

Colloidal silica, so-called ‘white carbon black’ is frequently used as an active filler in many polymer systems. Primary particles of silica are nanosized. However, their high surface energy and particularly the ability to form interparticle hydrogen

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bonds causes an aggregation or even agglomeration of silica in a polymer matrix. Many attempts have been made to prepare polymer nanocomposites filled with nanosilica. It is impossible to cause deaggregation of secondary particles with a high shear stress. To solve the problem, the method of nanosilica synthesis in a polymer matrix (*in situ*) was elaborated [6]. Tetraethoxysilane (TEOS) as a precursor is usually used [7]. To fasten the hydrolysis reaction, basic as well as acidic, catalytic systems could be added [8]. The first step of the process is the preparation of a TEOS–polymer mix. It is not so easy to prepare homogeneous mix because of a difference in solubilities of both components. As a consequence, a coalescence of TEOS molecules and formation of its droplets is often observed. After hydrolysis, micro- or mesoparticles of silica are formed. To avoid this detrimental effect, other precursors, reactive toward the polymeric matrix, are added to TEOS [9]. However, a full hydrolysis of precursors in polymer matrices is rather difficult. The same concerns the necessary separation of the hydrolysis product (e.g. ethyl alcohol) and residues of the catalytic systems applied. Therefore, in our opinion, the synthesis of nanosilica *in situ* is not a perspective method from the technological point of view.

Nanosilica could also be produced in a form of a dry powder via pyrolysis of tetraalkoxysilanes or tetrachlorosilane in the presence of water as well as by direct hydrolysis of sodium methasilicate or tetraalkoxysilanes. Stabilization of nanoparticles is needed to avoid their aggregation. Such products are already offered on the market, although their application in the polymer technology has been restricted so far because they aggregate during processing.

## 2. Preparation of silica from alkoxysilanes

Many important scientific and commercial applications of the sol-gel chemistry have already been developed [10]. Most sol-gel syntheses of silica are based on the hydrolysis of tetraalkoxysilanes, $Si(OR)_4$, according to the following equation, e.g.:

$$Si(OC_2H_5)_4 + 4H_2O \xrightarrow{\text{catalyst}} SiO_2 + 4C_2H_5OH$$

Gelation of silicon alkoxide solutions takes place as a result of the hydrolysis of the silicone alkoxides $Si(OR)_4$ and subsequent polycondensation (*dehydration*) leading to the formation of polymers and particles with siloxane bonds. The reaction can be expressed by the following formulae [11]:

$$Si(OC_2H_5)_4 + 4H_2O \xrightarrow{\text{catalyst}} Si(OH)_4 + 4C_2H_5OH$$

$$Si(OH)_4 \xrightarrow{\qquad} SiO_2 + 2H_2O$$

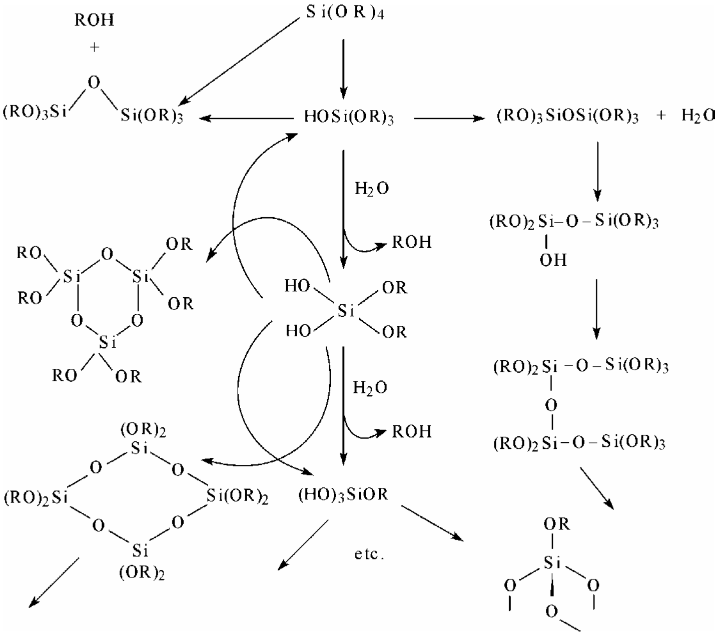
However, the mechanisms of these reactions are unknown because of the complexity of the gelation process. Theoretical reaction pathways are presented in Scheme 1, illustrating the competition between the hydrolysis and the condensation steps of some species, the number of which increases as the reactions proceeds [12]. Cyclic structures can be formed as well. The condensation between this kind of intermediate polyhydroxylated species may be responsible for the gel formation. The above reactions are catalyzed by acids or bases and are accompanied by the redistribution reactions:

$$2(RO)_3SiOH \rightleftharpoons (RO)_2Si(OH)_2 + (RO)_4Si$$

$$(RO)_2Si(OH)_2 \rightleftharpoons (RO)_3SiOH + ROSi(OH)_3$$

Thus, the proportions of Si–OH, $Si(OH)_2$, and $Si(OH)_3$ change during the process, which first gives a swollen gel. It is then dried, heated, and densified into the final monolithic piece of silica. The gelation may correspond to a crosslinking process taking place between macromolecular species of polysiloxanes containing free Si–OH bonds.

In the presence of acids, the probability of formation of $Si(OH)_4$, which is produced by the hydrolysis of all four OR groups of an alkoxide molecule, is small and condensation reactions start before the complete hydrolysis of $Si(OR)_4$ to $Si(OH)_4$ can occur. Under basic conditions $Si(OH)_4$ is easily formed by the preferential hydrolysis of the rest of the OR groups belonging to a partially hydrolyzed $Si(OR)_4$ molecule, and some silicon alkoxide molecules tend to remain non-hydrolized [11].



Scheme 1. Possible reactions of tetraalkoxysilanes

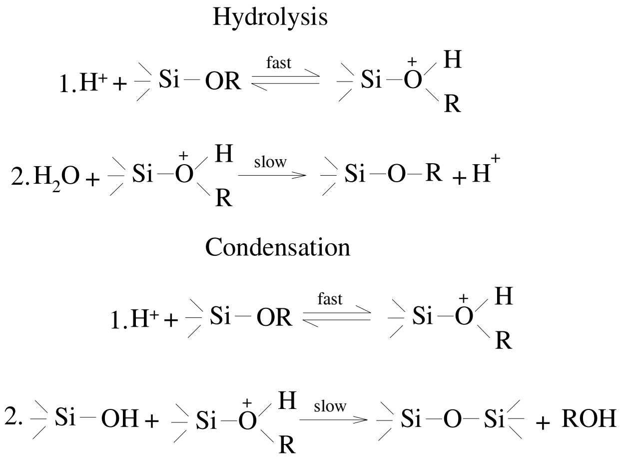
The determination of the overall mechanism of the chemical steps leading to gelation needs:

- information on the kinetics of all reactions involved at the beginning of the process [12];
- a better knowledge of the nature of 'building blocks' formed during the first steps.

The hydrolysis and condensation reactions involve a nucleophilic attack on the electrophilic silicon atom both in acid and basic catalysis, through the mechanisms depicted in Schemes 2 and 3 [13].

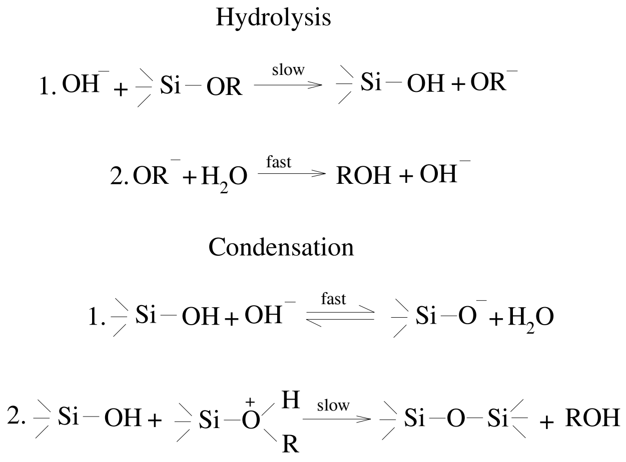
The catalyst and pH value of the solution, water concentration, silicon alkoxide concentration, the type of alkoxysilane and of solvent [11] affect the reaction rates, the reaction mechanism of the sol-gel transition, the gelation time, the nature of polymerized species formed in the sol, and the bulk nature of the gel.

The sol-gel process was also applied to two-phase systems, and thin films of uniform porous silica were successfuly made. Their structures depend on the precursor structure and deposition conditions [14]. It is possible to initiate the hydrolysis of TEOS without alcohol solvent by exposing TEOS and water to ultrasounds in the presence of an acid catalyst. The gelling time of the 'sonogel' was 115–200 min for different ratios of water per 1 mole of TEOS, while for classic gels, made by the dilution of 3 moles of alcohol per 1 mole of TEOS, the gelation may require several days [15].



Scheme 2. Acid catalysis

The combination of emulsion techniques with alkoxide hydrolysis offers a more versatile approach to preparing multicomponent oxide powders. Three general approaches can be applied. The first one involves preparation of water-in-oil emulsions, followed by the reaction of water droplets with alkoxide. In the second method, an aqueous sol is emulsified in an organic liquid and the sol droplets are then gelled. The third one involves emulsification of the alkoxide with an appropriate immiscible solvent, followed by addition of water to hydrolyze the alkoxide droplets [16].



Scheme 3. Basic catalysis

To form a stable emulsion, an addition of a surfactant is necessary in order to lower the interfacial energy and minimize the surface energy between two liquids. Emulsions formed with a solution consisting of 60% of mineral oil and 40% of heptane were stable with respect to alcohol generation, and powder formed without separation of the emulsion. After heating to 450 °C, residual mineral oil and unreacted alkoxide groups were burned off and the surface area increased from 2–8 $m^2/g$ to 220 –390 $m^2/g$. Densities of the silica particles (1.7 $g/cm^3$) were smaller than the theoretical ones also confirming a porous structure of $SiO_2$ [16].

The hydrolysis and polymerization of TEOS in ethanol solution containing water and ammonia allows preparation of monodispersed silica powders. The final particle size *d* was determined as a function of initial reagent concentrations over the range studied: 0.17–0.5 M TEOS, 0.5–3 M $NH_3$, 0.5–14 M $H_2O$ (at 25 °C). It was possible to obtain $SiO_2$ particles with average diameters between 15 and 700 nm [17].

The sol-gel method provides means for modifying glasses and crystalline ceramics with organic polymers [18–20], promising materials displaying unique and varied mechanical, electrical and optical properties. A wide variety of coatings compositions were produced by varying the ratio of PVDF-PTFE copolymer to TEOS and by varying the partial hydrolysis conditions of TEOS. The results of DSC indicated that polymer modified glasses contained regions of unrestricted polymer and regions in which the polymer and the glass were intimately mixed. Additions of relatively small amounts of TEOS to the copolymer increased the temperature of the onset of thermal decomposition – in some cases by as much as 40 °C. Similar unexpected increases in the temperature of thermal decomposition were observed in the previously studied PDMS-modified glasses. SEM studies of monoliths and coatings revealed variety of material microstructures. In many of the coatings, the honeycomb structures were observed [21]. SEM studies of PTFE–silicate composites showed that PTFE particles were wetted by TEOS, suggesting potential applications as adherent low-coefficient-of-friction coatings. The coefficient of sliding friction was reduced by incorporating PTFE into TEOS coatings, and heating was shown to improve the coating's resistance to wear [22].

Properties of the sol-gel glasses composed of $SiO_2$ [10] and $SiO_2$–$TiO_2$ [23] were also modified by addition of difunctional polydimethylsiloxane elastomeric oligomers in order to improve the fracture toughness [10]. Alternatively, the hydrolysis and polycondensation reactions of TEOS were carried out within a polymeric matrix, with the silica generated in the form of very small, well-dispersed particles. When the matrix is an elastomer, these particles provide the same highly desirable reinforcing effects obtained by the usual blending of a filler (such as carbon black) and polymer (such as natural rubber) prior to their being crosslinking or curing into tough elastomers of commercial importance. Various filling sequencies were applied, i.e. filler precipitation before or after curing [24].

## 3. Results and discussion

Based on the sources published as well as on our experience in the synthesis and application of conventional fillers, we came to the conclusion that there are three possible routes to avoid aggregation and agglomeration of primary nanosized silica particles:

- Synthesis of nanosilica in an oil or an oligomer liquid (using precursors with appropriately chosen substituents), which suppresses the process of grains enlargement because of a steric hindrance and lowers the tension at the interface. In such a case separation of reactions products is much easier as compared to the *in situ* method of synthesis. Also mixing of the nanosilica suspension in an oil or oligomer with a polymer could easily be performed.
- Synthesis of nanosilica in polymer latexes or during emulsion polymerization process. If the coprecipitation is carefully stirred, a uniform distribution of nanosilica in a polymer matrix can be achieved. A great advantage of the method is the possibility to obtain the dispersion of nanosilica in a powdered polymer system. The usage of filled polymer powders will increase due to more common application of extruders for the preparation of mixes instead of internal mixers.
- Synthesis of nanosilica functionalized on the surface. If appropriate precursors are used, functional groups cover the nanograins. In such a case, functional groups may be introduced into the top layer of nanograins, thus increasing the wettability of nanosilica by a polymer and also allowing their grafting by the matrix. In this article, some results of our experiments in this field are presented.

The syntheses of nanosilica in aliphatic or naphthenic oils and also in latexes of diene copolymers have been studied. We applied the sol-gel method and a new silane precursor of nanosilica, which was prepared by transesterification of tetraethoxysilane and (aminopropyl)trimethoxysilane with *n*-decyl alcohol in the presence of an emulsifier and a stabilizer.

Table 1. Reaction conditions and some results of nanosilica preparation

| Substrates [ml] | Synthesis | | | | |
|---|---|---|---|---|---|
| | A | B | I | II | III |
| 'Precursor'[a] (or TEOS) | 1.76 | 1.8 | 16.5 | (35.15) | 16.5 |
| Naphtenic oil (Nyfleks 221) | – | – | 16.5 | 10.0 | 5.5 |
| Aliphatic oil | (1.88) | (1.0) | – | – | – |
| Emulsifier (Rokanol) | – | – | 1.65 | 1.0 | 0.55 |
| 'Nanosilica stabilizing agent' (and as a second catalyst) | – | – | 0.20 | 0.20 | 0.20 |
| $H_2O$ | 0.04 | 0.02 | 0.85 | 11.35 | 0.85 |
| Temperature [°C] | ~ 25–30 | ~ 25–30 | ~ 25–80 | ~ 25–80 | ~ 25–30 |
| wt. % of $SiO_2$[b] | 15.9 | 26.2 | 14.6 | 37.4 | 33.3 |

[a] 'Nanosilica precursor' was prepared by transesterification of TEOS and 5 mol. % of (aminopropyl)trimethoxysilane with *n*-decyl alcohol.

[b] With respect to the substrate.

The goal of our studies was:

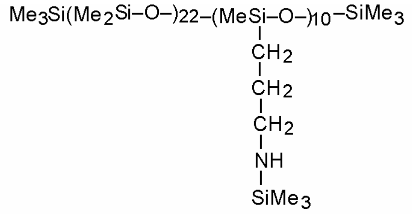
- Improvement of mechanical properties of elastomers (and other polymers) by decrease of the size of silica particles (as a filler) and formation of unconventional networks in an elastomer matrix or chemical bonding of silica with a polymer.
- Simultaneous improvement of surface properties of elastomers and other polymers (e.g., tribological properties, thermal stability) and decreasing their flammability.

The following assumptions were taken into consideration:

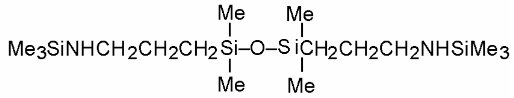
- Assurance of good homogeneity of the reagent system by chemical modification of TEOS, i.e. by substitution of one ethoxyl group with a group of fatty alcohol and synthesis of the so-called 'modified nanosilica precursor'.
- Regulation of sizes of molecules and particles of '$SiO_2$' by appropriate choice of the [$H_2O$]/['precursor'] stoichiometry and of the reaction conditions.
- Stabilization of silanol groups Si–OH by hydrogen bonds (using a stabilizing agent).
- Application of adhesion promoters.

As the main product we obtained transparent gels of nanosilica in oils with small amounts (a few per cent) of $SiO_2$ dispersions. The microscope and AFM studies confirmed the presence of particles of nanometric size. The nanosilica sols are currently applied to modification of properties of elastomers.

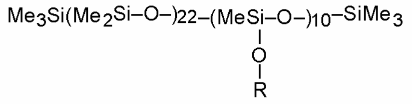
Our studies are continued in order to optimize reaction conditions and minimize the size of $SiO_2$ particles. Moreover, new hybrid modifiers of general formula $X(Me_2SiO)_4R$, where Me is the methyl group, and R a fatty alcohol radical ((1) X = H, R = $n$-$C_{10}H_{21}$; (2) X = RO = $n$-$C_{10}H_{21}$; (3) X = RO = $n$-$C_{18}H_{37}$) have been prepared. We have also prepared novel hybrid polymer modifiers containing polysiloxane units as side or terminal groups: trimethylsilylamino- functions and long chains of *n*-alkoxy- side groups (prepared by derivatization of polymethylhydrosiloxanes with fatty alcohols):



$Me_3Si(Me_2Si{-}O{-})_{22}{-}(MeSi(CH_2CH_2CH_2NHSiMe_3){-}O{-})_{10}{-}SiMe_3$



$Me_3SiNHCH_2CH_2CH_2Si(Me)_2{-}O{-}Si(Me)_2CH_2CH_2CH_2NHSiMe_3$



$Me_3Si(Me_2Si{-}O{-})_{22}{-}(MeSi(OR){-}O{-})_{10}{-}SiMe_3$

where: R = $n$-$C_{10}H_{21}$, $n$-$C_{14}H_{29}$, $n$-$C_{16}H_{33}$, $n$-$C_{18}H_{37}$

The chemical structures of new hybrid polysiloxanes were confirmed by spectroscopic methods: FT-IR and NMR ($^{1}$H-, $^{29}$Si-). Synthetic procedures will be published in a separate paper. These new products have been applied for the synthesis of modified silica nanoparticles in elastomers matrices (*in situ*). This way it is possible to modify surface and bulk properties of rubber vulcanizates. The studies of physical properties of rubbers obtained are in progress and will be published elsewhere.

## References

[1] *Organic-Inorganic Nanocomposite Materials*, [in:] Chem. Mater., 13 (2001), No. 10.

[2] Put J., *e-Polymers*, T_001[2002].

[3] Furukawa M., Yashikai K., Proceedings of the International Rubber Conference, Prague, July 2002.

[4] Rong M.Z., Ji Q.L., Zhang M.Q., Friedrich K., Eur. Polymer J., 38 (2002), 1573.

[5] (a) Alexandre M., Dubois P., Mater. Sci. Eng., Reports, 28 (2000), 1.
(b) Kang S., Hong S.I., Choe C.R., Park M., Rim S., Kim J., Polymer, 42 (2001), 879.

[6] (a) Mark J.E., Ning Y.-P., Jiang C.Y., Tang M.-Y., Roth W.C., Polymer, 26 (1985), 2069.
(b) Mark J.E., Heteroorg. Chem. Rev., 3 (1996), 307.

[7] Iler R.K., *The Chemistry of Silica*, Wiley, New York, 1979.

[8] Stoeber W., Fink A., Bohn E., J. Colloid Interface Sci., 26 (1968), 62.

[9] Schartl W., Gohr K., Graf C., Lindenblatt G., Ross C., Scmid M., *Extended Abstracts of the Silica '98* Conference, Mulhouse, 1998, p. 427.

[10] McGrath J.E., Pullockaren J.P., Riffle J.S., Kilic S., Elsbernd C.S., [in:] *Ultrastructure Processing of Advanced Ceramics*, J.D. Mackenzie, D.R. Ulrich (Eds.), Wiley, 1984, Chapter 3, pp. 55–75.

[11] Sakka S., Kozuka H., Kim S.-H., [in:] *Ultrastructure Processing of Advanced Ceramics*, J.D. Mackenzie, D.R. Ulrich (Eds.), Wiley, 1984, Chapter 10, pp. 113–126.

[12] Kaźmierski K., Ph. D. Thesis, Łódź, 1996.

[13] Corriu R.J.P., Leclerq D., Vioux A., Pauthe M., Phalippou J., [in:] *Ultrastructure Processing of Advanced Ceramics*, J.D. Mackenzie, D.R. Ulrich (Eds.), Wiley, 1984, Chapter 7, pp. 113–126.

[14] Brinker C.J., Hurd A.J., Ward K.J., [in:] *Ultrastructure Processing of Advanced Ceramics*, J.D. Mackenzie, D.R. Ulrich (Eds.), Wiley, 1984, Chapter 15, pp. 223–239.

[15] ELSQUIAS L., ZARZYCKI J., [in:] *Ultrastructure Processing of Advanced Ceramics*, J.D. Mackenzie, D.R. Ulrich (Eds.), Wiley, 1984, Chapter 17, pp. 255–270.

[16] HARDY A.B., GOWDA G., MCMAHON T.J., RIMAN R.E., RHINE W.EBOWEN., H.K., *Ultrastructure Processing of Advanced Ceramics*, J.D. Mackenzie, D.R. Ulrich (Eds.), Wiley, 1984, Chapter 30, pp. 407–428.

[17] BOGUSH G.H., ZKOSKI C.F., [in:] *Ultrastructure Processing of Advanced Ceramics*, J.D. Mackenzie, D.R. Ulrich (Eds.), Wiley, 1984, Chapter 35, pp. 477–486.

[18] SCHMIDT H., U.S. Patent 4 374 696.

[19] MARK J.E., JIANG C.Y., TANG M.-Y., Macromolecules, 17, (1984), 2613.

[20] HUANG H.H., ORLER B., WILKES G.L., Polym. Bull., 14 (1985), 557.

[21] DOYLE W.F., FABES B.D., ROOT J.C., SIMMONS K.D., CHIANG Y.M., UHLMANN D.R., [in:] *Ultrastructure Processing of Advanced Ceramics*, J.D. Mackenzie, D.R. Ulrich (Eds.), Wiley, 1984, Chapter 61, pp. 795–805.

[22] DOYLE W.F., UHLMANN D.R., [in:] *Ultrastructure Processing of Advanced Ceramics*, J.D. Mackenzie, D.R. Ulrich (Eds.), Wiley, 1984, Chapter 78, pp. 953–962.

[23] PARKHURST C.S., DOYLE W.F., SILVERMAN L.A., SINGH S., ANDERSEN M.P., MCCLURG D., WNEK G.E., UHLMANN D.R., [in:] *Better Ceramics Through Chemistry*, C.J. Brinker, D.E. Clark, D.R. Ulrich (Eds.), Materials Research Society Symposium Proceedings, Pittsburgh (PA), 1986, Vol. 73, pp. 769.

[24] MARK J.E., [in:] *Ultrastructure Processing of Advanced Ceramics*, J.D. Mackenzie, D.R. Ulrich (Eds.), Wiley, 1984, Chapter 46, pp. 623–633.

*Received 12 June 2003*
*Revised 23 July 2003*