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Research Article

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Synthesis and characterisation of poly (pyrrole-co-isoniazid)

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ABSTRACT

Poly (pyrrole-co-isoniazid) was prepared by electrochemical and chemical oxidative polymerization. Homo polymer of pyrrole and copolymer thin films of pyrrole and isoniazid were synthesized by using cyclic voltammetry with 0.1M KCl in acetonitrile medium on the surface of the glassy carbon electrode. The copolymer formation, their electrochemical behaviour were studied. The analogous copolymer was prepared via a chemical oxidative polymerization in 1M HCl in the presence of potassium persulphate as oxidant. The structure of the copolymer was systematically studied by IR, NMR and X-ray powder diffraction (XRD) methods and the surface morphology with SEM analysis.

Keywords: Copolymerization, Isoniazid, Pyrrole, Cyclic voltammetry, Glassy carbon electrode.

INTRODUCTION

The synthesis of conducting polymer films for various applications like electrochromic devices [1], photo electrochemical devices [2], rechargeable batteries [3] and corrosion protection [4-7] were frequently involved structural modification of the polymer backbone to enhance the properties. Incorporation of various functional groups changes the conductivity and porosity. Polyaniline, polypyrrole and their derivatives have been regarded as the most important conducting polymers due to their stability and synthetic advantages [8, 9]. The electropolymerization of aniline and its derivatives brings about some difficulties like slow nucleation and film growth, but its high stability and interesting electrochemical properties have attracted much attention [10]. On the other hand, polypyrrole films generally exhibit better conductivity and can be more easily synthesized by electropolymerization than polyaniline [11, 12]. Some works have been reported the copolymerization of pyrrole with aniline and thiophene derivatives [13-16].

Copolymerization is a simple way of preparation of new polymers, and it greatly increases the scope of tailor-making materials with specifically desired properties [17]. The copolymerization potential of two different monomers plays an important role in the properties of a copolymer [18]. The monomer concentration ratio can readily control the copolymerization potential of two monomers [19]. Among the various techniques available for the electrochemical synthesis of conducting polymers, the cyclic voltammetry (CV) has been used for the fast production of the good quality polymer films [20].

Isoniazid (CAS: 54-85-3) is a widely used drug alone in the prophylaxis and in combination with other anti-tuberculars' in the treatment of all forms of tuberculosis [21]. In the present investigation, the cyclic voltammetry (CV) was employed for the electrochemical copolymerization of pyrrole and isoniazid. The growth behaviour of copolymer film on GC surface was studied. The copolymers were also synthesized by chemical oxidative polymerization and characterised.

EXPERIMENTAL SECTION

2.1. Materials

The pyrrole was distilled under reduced pressure and isoniazid (Sigma-Aldrich) was recrystallised from methanol. 0.1M isoniazid stock solution was prepared in 50% aqueous ethanol. Potassium persulphate (Merck), sulphuric acid and methanol (Merck) were used as received. All the chemicals were of analytical reagent grade and the solutions were prepared using double distilled water.

2.2. Synthesis of copolymer of pyrrole and isoniazid

2.2.1. Electrochemical polymerization

Electrochemical polymerization was carried out using CH Electrochemical analyser model 620D instrument equipped with a three electrode single compartment cell assembly. A glassy carbon (GC) disc working electrode of area 0.0314 cm^2, an Ag/AgCl reference electrode and a platinum wire as counter electrode were used. The homo and copolymerization was carried out in acetonitrile medium with 0.1M KCl as supporting electrolyte. The homopolymer of pyrrole and copolymers of pyrrole and isoniazid films were deposited by CV technique with 30 cycles. Throughout the studies, oxygen free atmosphere was maintained with purified nitrogen gas atmosphere.

2.2.2. Chemical copolymerization

Copolymer of poly (pyrrole-co-isoniazid) was chemically synthesized using potassium persulphate as initiator in an aqueous acidic medium at 0-4^{0}C in a similar manner to that previously described [22-24]. A typical procedure for preparation of the copolymer is as follows.

Monomers, pyrrole 0.5M and isoniazid 0.1M in a 50 ml of 1 M HCl solution was cooled to 0-4^{0}C. 10ml of 0.25M potassium persulphate in 1 M HCl was cooled to 0-4^{o}C. Then the oxidant, potassium persulphate solution was added drop wise to the monomers solution for 1 hour with constant stirring in nitrogen atmosphere at 0-4^{o}C. After the addition of the oxidant, stirring was continued for another 6 hours to ensure the completion of the reaction. A dark bluish green precipitate was obtained. The copolymer precipitate thus obtained was filtered, washed with distilled water until the filtrate became colourless and finally with methanol. It was dried in an air oven at 60^{o}C for 5 hours.

RESULTS AND DISCUSSION

3.1. Copolymerization of pyrrole and isoniazid

3.1.1. Electrochemical behaviour of isoniazid

The cyclic voltammetry of 0.09 M isoniazid in 0.1 M aqueous sulphuric acid medium (pH 1.0) with a potential range from 1.5 V to -1.2 V with different scan rates from 100 mV/sec to 500 mV/sec. was studied. The cyclic voltammogram showed a well defined reduction peak around -850 mV and an oxidation peak around 1400 mV (Fig. 1.). The cyclic voltammetric studies reveal that the electrons transfer process is an irreversible diffusion controlled one.

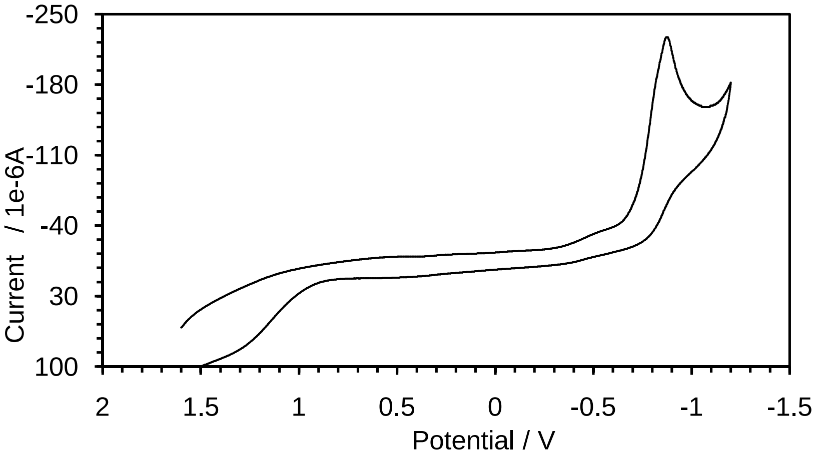

Fig-1. Cyclic voltammetry of 0.09 M isoniazid on GCE in 0.1M H_2SO_4 at a scan rate of 100 mV/s

3.1.2. Electrochemical behaviour of pyrrole

The cyclic voltammogram of 0.01 M pyrrole in 0.1M KCl/acetonitrile medium (pH 7.0) on a stationary glassy carbon electrode with a potential range from 0.6V to –1.0V at a scan rate of 100 mV/sec is shown in Fig.2.

The voltammogram showed an anodic peak at 0.22V. The peak current gradually increased for every cycles and the peak potential was shifted cathodically. After completion of the 20 cycles, a dark bluish colour polymer film on the working electrode was observed.

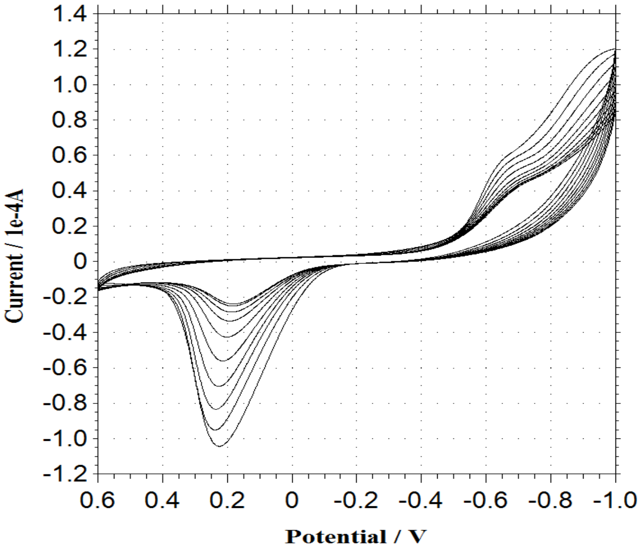

Fig-2. Cyclic voltammetry of 0.01M pyrrole on GCE in 0.1M KCl /acetonitrile medium at a scan rate of 100 mV/s

3.1.3. Electrochemical behaviour of isoniazid with pyrrole

The monomers of 0.01 M pyrrole and 0.005 M isoniazid was carried out on GCE in acetonitrile by repeated potential cycling between 0.6 and -1.0 V. The cyclic voltammogram shows an anodic peak entered at a potential of 0.3V in the first cycle. (Fig-3).

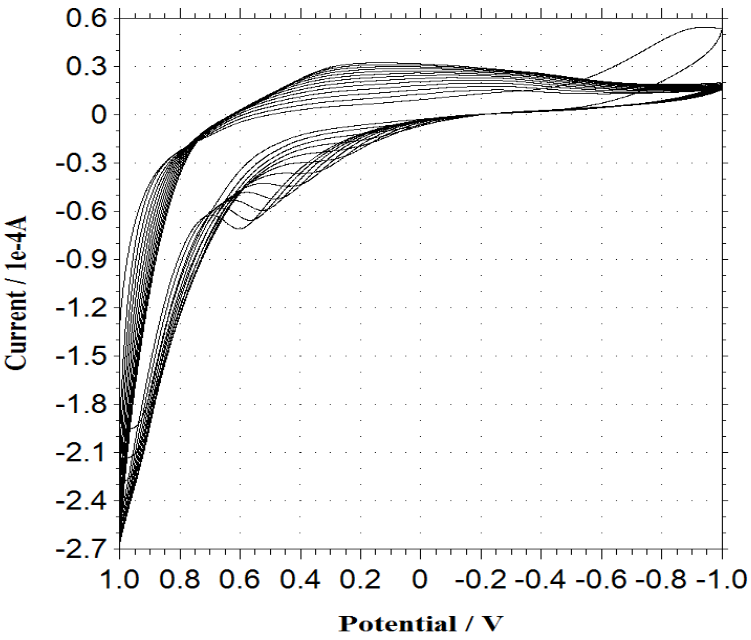

Fig-3. Cyclic voltammetric behaviour of 0.01M pyrrole and 0.005M isoniazid on GCE in 0.1M KCl /acetonitrile medium at scan rate of 100 mV/s

When the cycling process continued, the cathodic and anodic currents were increased gradually and the anodic peak shifted anodically and the cathodic peak shifted cathodically for every cycle. The anodic peak observed at 0.22V in the homopolymerisation of pyrrole was shifted anodically in each cycle of the copolymerization of pyrrole and isoniazid. The bluish green colour film was seen on the working electrode. These behaviours suggest the formation of the copolymer pyrrole-co-isoniazid.

3.2. FT-IR spectral analysis of poly (pyrrole-co-isoniazid)

The IR spectral analysis of poly(pyrrole-co-isoniazid) is shown in Fig- 4

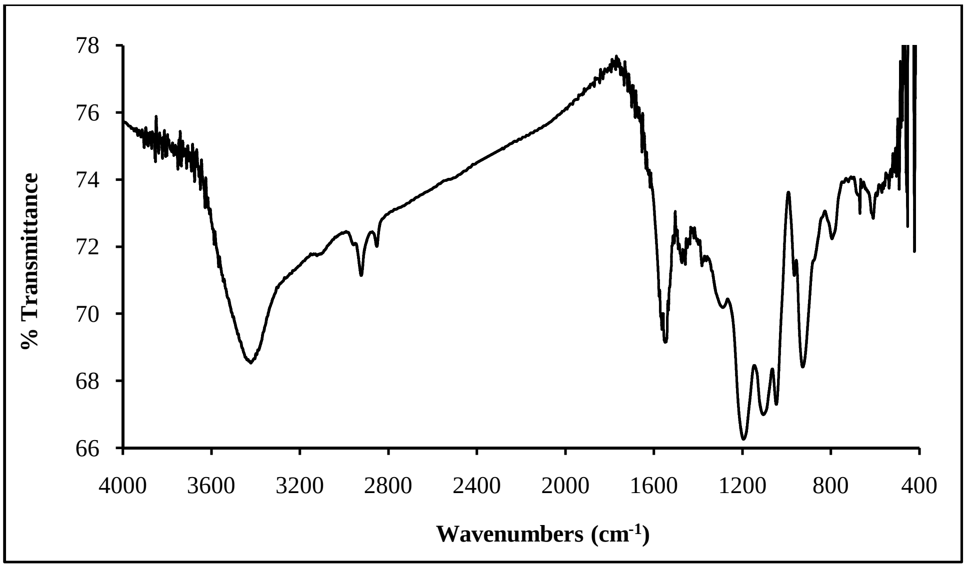

Fig-4 FT-IR spectra of Poly(pyrrole-co-isoniazid)

The band observed at 3421.48 cm^{-1} is attributed to the N-H stretching, since both monomer units contain $-NH_2$ and N-H groups. The bands observed around 2960, 2822 cm^{-1} is attributed to the C-H stretching and anti-symmetric stretching aromatic.

A prominent band at 1559.84 cm^{-1} is attributed to aromatic pyridyl C=N stretching. The band observed at 1195.95 cm^{-1} is assigned as the C-N stretching of aromatic secondary amine. The occurrence of band at 1046.41 cm^{-1} assigned as carbon ring in cyclic, the band at 669.30 cm^{-1} assigned as C-N-C bending. The broad band around 3106 cm^{-1} is due to the involvement of $-NH_2$ group in one of the monomer in intermolecular electrostatic binding.

The predominant band for carbonyl (C=O) which is present in the monomer at 1710 cm^{-1} is vanished in the copolymer. This clearly shows that these copolymers are linked through the carbonyl (C=O) unit of isoniazid in the copolymer. The band observed at 490 cm^{-1} is attributed to the C-N-C bend stretching in aromatic amine.

The above results in the IR spectral data's of copolymer demonstrate that an electrochemical copolymerization of pyrrole and isoniazid took place most probably at the given conditions. The IR spectrum of the copolymer indicates that there are the $-NH_2$ group, –NH group and C-N-C in the copolymer film. Thus, the pyrrole and isoniazid units are contained in the copolymer.

3.3. ^{1}H NMR spectral analysis of poly(pyrrole-co-isoniazid)

The ^{1}H NMR spectra of poly (pyrrole-co-isoniazid) given in Fig. 5. The main peaks are discussed here.

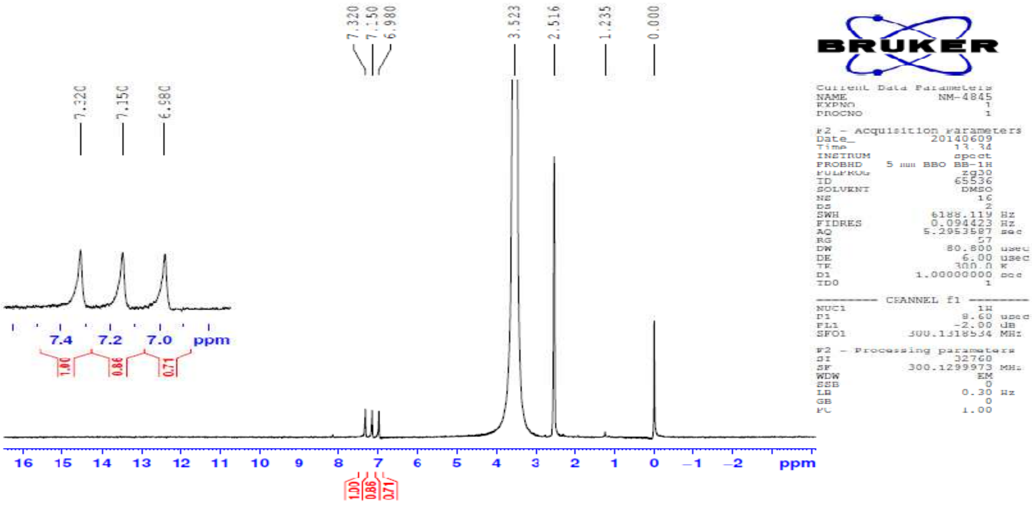

Fig-5 ^{1}H NMR spectra of poly(pyrrole-co-isoniazid)

The signals around 7 and 7.2 -7.4 ppm are attributed due to respective aromatic protons. The signal at 3.55 ppm can be attributed to the N-H protons and secondary amine. The signals at the region 2.5 – 3.5 ppm can be again attributed to the aromatic substituted NH and NH_2 protons. Based on the IR and ^1H NMR spectra, it is concluded that the polymer deposited on the working electrode is a copolymer.

3.4. XRD studies of poly(pyrrole-co-isoniazid)

The X-ray diffraction analysis is a powerful tool to determine the structure and crystallization of polymer matrices. The phase in which the polymer chains are parallel and ordered in close packed array is the crystallites region, whilst the phase where the chains are not ordered and do not have parallel alignment is the amorphous region. This ordered arrangement of polymer chains in the crystalline phase may be of different types depending on the nature of the polymer and can be detected from X-ray diffraction. Fig. 6 shows X-ray diffraction pattern of poly (pyrrole-co-isoniazid)

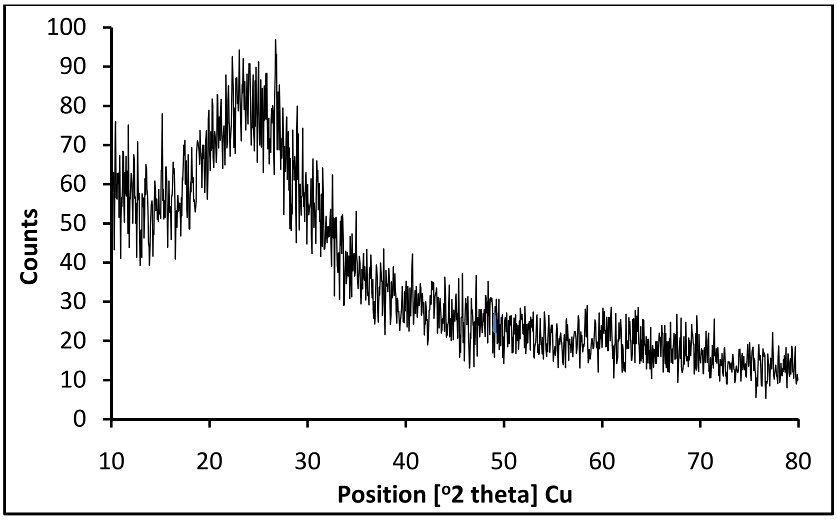

Fig-6. X-ray diffraction pattern of poly (pyrrole-co- isoniazid)

The XRD patterns of the poly (pyrrole-co-isoniazid) seems to be comprised with one broad peak was observed at about $2\theta = 24^{\circ}$ and do not show any sharp peak characteristics of a crystalline materials. Careful analysis of X-ray diffraction of poly (pyrrole-co- isoniazid) suggests that it has amorphous nature.

3.5. Morphology of poly (pyrrole-co- isoniazid)

Scanning electron micrographs (SEM) of the copolymer provide a clear morphology of the copolymer. The SEM images of the poly (pyrrole-co-isoniazid) is shown in Fig-7

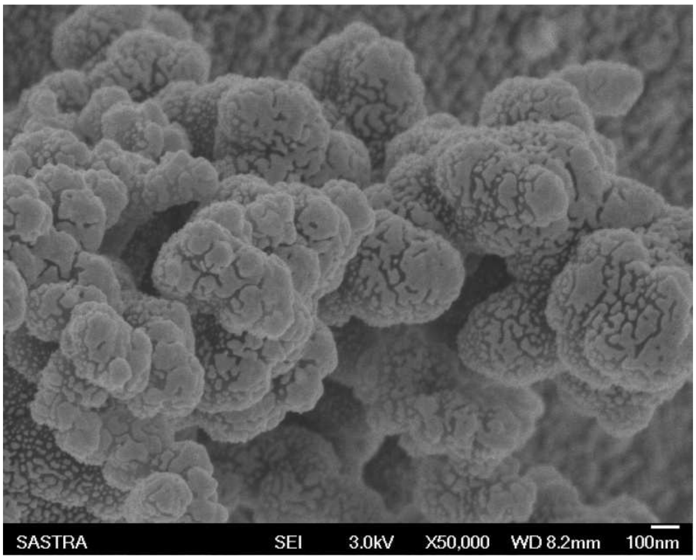

Fig-7 SEM images of the poly (pyrrole-co-isoniazid)

The scanning electron micrographs show a nanostructure with homogeneous sponge like textured nano porous surface. The SEM morphology obtained indicates the presence of polymer overgrowth leading to agglomeration.

CONCLUSION

The poly (pyrrole-co-isoniazid) was synthesized by cyclic voltammetry in 0.1M KCl/acetonitrile medium on the surface of the glassy carbon electrode. The analogous copolymers were synthesised via a chemical oxidative polymerization in 1M HCl in the presence of potassium persulfate as an oxidant. The formation of copolymer was supported by IR, ^{1}H NMR studies. The participation of -C=O group in the formation of poly (pyrrole-co-isoniazid) is supported by IR results. X-ray powder diffraction (XRD) studies clearly indicate the amorphous nature of the copolymer. Homogenous nano porous surface morphology was established by SEM analysis.

REFERENCES

[1] V Prevost; A Petit; F Pla. *Synth. Met.*, **1999**, 104(2), 79-87.
[2] C Özdemir; H Kaplan Can; N Çolak; A Güner. *J. Appl. Polym. Sci.*, **2006**, 99(5), 2182-2192.
[3] T Jeevananda; Siddaramaiah; S Seetharamu; S Saravanan; Lawrence D'Souza. *Synth. Met.*, **2004**, 140(2-3), 247-260.
[4] SM Chen; YH Fa. *J. Electroanal. Chem.*, **2003**, 553, 63-75.
[5] DD Borole; UR Kapadi; PP Mahulikar; DG Hundiwale. *Mater. Lett.*, **2006**, 60(20), 2447-2452.
[6] P Herrasti; FJ Recio; P Ocón; E. Fatás. *Prog. Org. Coat.*, **2005**, 54(4), 285-291.
[7] SU Rahman; MA Abul-Hamayel; BJ Abdul Aleem. *Surf. Coat. Technol.*, **2005**, 200(9), 2948-2954.
[8] T Tüken; B Yazıc; M Erbil. *Mater. Des.*, **2007**, 28(1), 208-216.
[9] T Tüken; G Tansuğ; B Yazıcı; M Erbil. *Prog. Org. Coat.*, **2007**, 59(1), 88-94.
[10] DD Borole; UR Kapadi; PP Mahulikar; DG Hundivale. *Mater. Lett.*, **2004**, 58(29), 3816-3822.
[11] BC Roy; MD Gupta; JK Ray. *Macromolecules,* **1995**, 28(6), 1727-1732.
[12] XG Li; MR Huang; LX Wang; MF Zhu; A Menner; J Springer. *Synth. Met.*, **2001**, 123(3), 435-441.
[13] JW Kim; CH Cho; F Liu; HJ Choi; J Joo. *Synth. Met.*, **2003**, 135-136, 17-18
[14] M Sato; K Amano; H Ishikawa. *Jpn. Pat.* 07 – 118371, 1995.
[15] Y Wei; J Tian; KF Hsueh. *Polym. Mater. Sci. Eng.*, **1994**, 71, 586-587.
[16] W Czetrwinski; G Wrzeszcz; K Kania; JF Rabek; LA Linden. *J. Mater. Sci.*, **2000**, 35(9), 2305-2310.
[17] MM Ghoneim; KY El-Baradie; A Tawfik. *J. Pharm. Biomed. Anal.*, **2003**, 33(4), 673-685.
[18] A Bagheri; MR Nateghi; A Massoumi. *Synth. Met.*, **1998**, 97(2), 85-89.
[19] P Manisankar; C Vedhi; G Selvanathan; RM Somasundaram. *J. Chem. Mat.*, **2005**, 17(7), 1722-1727.
[20] Shaolin Mu, *Synth. Met.*, **2004**, 143(3), 259-268.
[21] USP DI®, Drug Information for the Health Care Professional, Vol. I, 15th ed., **1995,** 1627.
[22] AD Borkar; MC Gupta; SS Umare. *Polym. Plast. Technol. Eng.*, **2001**, 40(2), 225-234.
[23] AD Borkar; SS Umare. *Int. J. Chem. Sci.*, **2010**, 8(2), 1110-1120.
[24] AD Borkar; SS Umare; PB Heda. *Mat. Res. Innovations*, **2011**, 15(2), 135-139.