

MECHANOCHEMICAL SYNTHESIS OF FULLERENE DERIVATIVES AND THEIR PROPERTIES

Arbuzov A.A.*, Muradyan V.E.

Institute of Problem of Chemical Physics RAS,
1 Acad. Semenov's av., Chernogolovka, 142432 Russia
*Fax: (+7)(496)5155420 E-mail: arbuzov@icp.ac.ru

Introduction

Introduction of fullerenes into various polymeric matrixes is one of perspective ways of their modification with the purpose of improvement of electromagnetic, physicochemical and other properties of polymers. For investigation of fullerenes influence on physicochemical properties of films of polyvinyl alcohol (PVA) water-soluble fullerene derivatives have been synthesized.

Results and discussion

One of the water-soluble derivatives fullerene is fulleranol (FOL) which containing up to 27 groups on one molecule of fullerene C_{60} [1–3]. Fullerene C_{60} and a mixture of fullerenes C_{60}/C_{70} as a dry toluene extract of the fullerene-containing soot prepared by arc-discharge method was used. [4] Fullerenols received by the technique developed by mechanochemical synthesis in planet-ball mill at addition KOH. In the IR spectrum of fulleranol observed the maximum of absorption described in the different articles at 1607, 1376 and 1076 cm^{-1} (Fig. 1). Presence of a maximum of absorption in the field of 1712 cm^{-1} (bond $C=O$) speaks formation of ketal form of fulleranol as a result of neutralization KOH by a hydrochloric acid. [5]

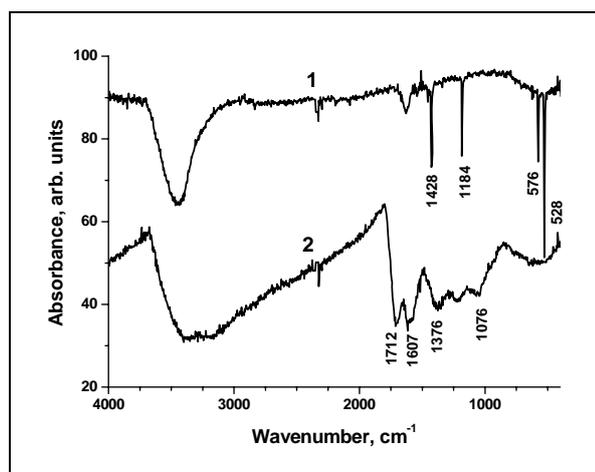


Fig. 1. IR spectra of fullerene C_{60} (1) and fulleranol (2).

Results of the element analysis have shown a conservative value contents of carbon at the rate of on formula $C_{60}(OH)_{26}$ and the contents of oxygen

is higher. It can be connected to presence in FOL of oxygen bridge $C_{60}-O-C_{60}$.

After mechanochemical processing C_{60} at presence $LiNH_2$ (LA) and the subsequent hydrolysis, formation of adduct containing both OH- and NH_2 -groups was supposed. In the IR spectrum received adduct are observed all maximums of absorption characteristic for FOL and also at 1041 and 769 cm^{-1} which it is possible to explain presence in adduct of bonds C-N and N-H respectively. Results of the element analysis have shown that in received adduct on one molecule C_{60} it is necessary 9 OH- and 4 NH_2 -groups.

In result C_{60} mechanochemical processings with sulfanilic acid (SAA) also it has been received water-soluble fullerene derivative. For production of water-soluble fullerene derivatives both with aminobenzoic acid (ABA) and aminocaproic acid (ACA) required addition KOH into reaction mixture. The received materials have been characterized by IR spectroscopy and thermogravimetry. By results of the element analysis of adducts C_{60} with ABA, ACA and SAA the quantity attached to fullerene groupings which on the average makes 4, 2 and 6 molecules of corresponding amino acid is determined. The sulfur content appeared twice less than calculated under formula $C_{60}(NHC_6H_4SO_3H)_6$, thus only 3 from 6 joined groupings had sulfonics groups.

For research of modifying influence of the produced C_{60} fullerene derivatives have been received PVA film for corresponding water solutions by a sprinkling method on a glass substrate. The contents of adducts in PVA varied from 0.1 up to 1 %. Physicochemical tests carried out on a series from 5 PVA films $5 \times 70 \times 0.1$ mm.

Dependences of breaking strength (σ), percentage elongation (ΔX) and the module of elasticity (E) from contents of FOL and adduct C_{60} -ACA had extreme character and achieved a maximum at the content 0.2 and 0.5 wt.% respectively (Tabl. 1). The received results testify that FOL and adduct with ACA together with increase in strength also play a role of softeners.

Table. 1. Physicomechanical properties PVA films modified of FOL and adduct C₆₀-ACA.

	$\omega,^* \%$	E, MPa	σ , MPa	$\Delta X, \%$
	0	4740	107	4.69
FOL	0.1	5090	128	5.26
	0.2	5840	144	5.93
	0.5	4940	129	5.65
	1	4900	113	4.42
Adduct C ₆₀ -ACA	0.1	4780	108	4.13
	0.2	5120	116	3.84
	0.5	5230	121	4.35
	1	4560	110	4.30

* ω – content of adduct in PVA films

Addition to PVA 0.1 wt.% of an adduct C₆₀-LA has led to sharp reduction of the elasticity module with 4730 up to 2540 MPa and breaking strengths with 108 up to 47 MPa. At further increase in concentration of adduct strength films increases, but does not reach initial value.

Breaking strength of PVA films modified adducts of C₆₀ fullerene with SAA and ABA increase with growth of concentration of the modifier and at 1 wt.% adduct achieve 132 MPa and 112 MPa respectively, whereas for unmodified PVA film - 107 MPa.

Table. 2. Physicomechanical properties PVA films modified of adducts C₆₀ with SAA or ABA.

	$\omega, \%$	E, MPa	σ , MPa	$\Delta X, \%$
	0	4730	107	4.69
Adduct C ₆₀ -SAA	0.1	4410	122	6.01
	0.2	4790	125	4.84
	0.5	5120	128	4.21
	1	5300	132	3.82
Adduct C ₆₀ -ABA	0.1	4670	107	4.85
	0.2	4590	109	5.02
	0.5	4920	110	4.43
	1	5220	112	3.25

However percentage elongation of films modified by these adducts decreases with growth of their concentration. Thus adducts C₆₀ fullerene both with SAA and ABA increase strength of PVA films worsening their deformation properties.

Conclusions

In this work it was developed the technique of mechanochemical synthesis of water-soluble derivatives of fullerene, characterized by the element analysis, IR spectroscopy and thermogravimetry. The produced derivatives have been investigated as modifiers of polyvinyl alcohol films. Influence of derivatives on strength properties of PVA films was shown already at concentration of 0.1-0.2 wt.%.

References

1. Li J, Takeochi A, Ozawa M et al. C₆₀ Fullerol Formation Catalysed by Quaternary Ammonium Hydroxides. *J. Chem. Soc., Chem. Comm.* 1993;: 1784–1785.
2. Wang Sh., He P. et. al. Novel and Efficient Synthesis of Water-Soluble [60]Fullerenol by Solvent-Free Reaction. *Synthetic Communications* 2005;35:1803–1808.
3. Alves G., Ladeira L. et. al. Synthesis C₆₀(OH)₁₈₋₂₀ in Aqueous Alkaline Solution Under O₂-Atmosphere. *J. Braz. Chem. Soc.* 2006;17:1186–1190.
4. Kushch S.D., Muradyan V.E., Moravskii A.P., and Fursikov P.V. Activation of methane on fullerene black. *Neftekhimiya* 1997;37:112–118.
5. Chiang L, Upasani R, Swirczewski J. Evidence of Hemiketals Incorporated in the Structure of Fullerols Derived from Aqueous Acid Chemistry. *J. Am. Chem. Soc.* 1993;115:5453–5457.