

# Investigation of polymer membranes modified by fulleranol for dehydration of organic mixtures

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**Abstract.** This study focuses on the development of novel dense and supported mixed-matrix membranes based on chitosan and poly(2,6-dimethyl-1,4-phenylenoxide) (PPO) with low-hydroxylated fulleranol C<sub>60</sub>(OH)<sub>12</sub>. These novel membranes containing nano-carbon particles were prepared to reach high membrane performances for further integration in a dehydration process like distillation coupled with pervaporation. SEM microscopy was used to visualize the internal morphology of the membrane. It was found that all membranes were well stable and highly water-selective in spite of the different nature of polymers.

## 1. Introduction

At the present time the membrane processes are of significant technological and economic importance in the chemical industry. Membrane methods are highly demanded in various industries for purification, concentration and separation of liquid and gaseous mixtures due to the compactness of the equipment, environmental friendliness and low energy consumption. One of the most promising processes for the separation of low-molecular liquid mixtures is the pervaporation. This membrane method is a low-energy, waste-free and environmentally friendly way of separating various mixtures: azeotropic mixtures, mixtures of isomers, and also close-boiling and thermally unstable substances. The operational characteristics of this method make it attractive to the chemical, petrochemical, biochemical, pharmaceutical industry, as an alternative method of separation by modern methods.

Rapid development of membrane technology requires the creation of new materials with improved characteristics. One of the promising methods to get tailoring physico-chemical and transport characteristics of membrane materials is the modification of known polymers by carbon materials, i.e., the creation of membranes with a mixed matrix.

Previous works showed the relevance of the use of fullerene and its water-soluble derivatives to improve the transport properties of pervaporation membranes as a modifier [1,2] and a cross-linking agent [3–5].

Two different types of polymeric materials were chosen as polymers: chitosan, a well-known hydrophilic polymer and polyphenylene oxide, a hydrophobic polymer.

Many studies [6–11] are aimed at the study of chitosan as a membrane material because of its unique physico-chemical characteristics: high affinity for water, good film-formability, mechanical and chemical stability. However, chitosan-based membranes often have low selectivity due to excessive swelling in the water. To reduce the degree of swelling of chitosan in water, various methods of cross-linking the polymer (physical, chemical) are used, using, as a rule, toxic or ineffective cross-linking reagents (sulfuric acid, alkali, glutaraldehyde, acrylic acid, etc.). One of the most promising directions in this area



is the modification and functionalization of the polymer by nanoparticles. In this paper, fullereneol  $C_{60}(OH)_{12}$  particles were as cross-linking agent. This choice was based on the previous studies on modification of PVA by fullereneol [3–5].

Polyphenylene oxide (PPO) is a glassy polymer with good film-forming and mechanical properties, which has thermal stability and chemical stability in solutions of alkalis, mineral acids and salts, in superheated steam environment, racks under radioactive irradiation and the action of microorganisms. Conversely to chitosan, this polymer does not swell extensively in water or protic solvents. In diffusion processes of separation, PPO exhibits properties as one of the most permeable glassy polymers especially for water. However, this polymer has a relatively low selectivity in the separation processes. Previously, attempts were made to improve the separation factor of PPO using laborious and unsafe methods of chemical modification of this polymer (sulfonation, bromination, alkylation, etc.) [12,13], but these methods have not found industrial applications to date. In the previous studies it was shown that in spite of hydrophobic nature of PPO under pervaporation separation of ethanol-water mixtures the main component of the permeate was water according to the mechanism described in [14]. In this work, the modification of the PPO by a nanoparticle (fullereneol  $C_{60}(OH)_{12}$ ) has been studied with the aim to improve further the transport properties of membranes due to OH-groups of water fullerene particles.

Therefore, the purpose of this study was to create a mixed-matrix membranes, characterizing their structural and transport properties in pervaporation.

## 2. Experimental part

### 2.1. Materials

Chitosan with medium molecular weight and poly (2,6-dimethyl-1,4-phenylenoxide) (PPO) were purchased from Sigma-Aldrich (USA) and used as the membrane materials.  $C_{60}(OH)_{12}$  (Fullerene Technologies, Russia) was used for polymer modification. A porous membranes based on aromatic polysulfone amide (UPM, pore size 200 Å) and on copolymer of vinylidene fluoride (fluoroplastic F42L) and tetrafluoroethylene (MFFC, pore size 0.05 μm) were purchased from Vladipor (Russia) and a porous membrane based on polyacrylonitrile (PAN, pore size 200 Å) was purchased from Vladipor (Germany) and used as membrane supports. Ethanol and tetrahydrofuran (THF) was purchased from ZAO Vecton (Russia).

### 2.2. Preparation of chitosan and chitosan-fullereneol membranes

**2.2.1. Preparation of composites.** The chitosan-fullereneol composites were prepared by mixing solutions of chitosan in 1 wt.% acetic acid aqueous solution and fullereneol in water in amounts that provided the required content of fullereneol in the composite (up to 1 wt.%). The resulting solution was allowed to stand for 3-4 days for interactions to take place between the polymer and fullereneol molecules. Next, the composite solution was sonicated for 40 min.

**2.2.2. Preparation of membranes.** Dense membranes based on chitosan and fullereneol-chitosan composites with the thickness ~ 40 μm were obtained by casting a 1 wt.% polymer solution on a Petri dish. The solvent was removed by evaporation at 40 °C; the membrane was separated from the substrate and dried in a vacuum oven at 40 °C up to the constant weight. Then the membranes based on parent polymer and its composite were subjected to heat treatment at 140 °C during 100 min for cross-linking.

The formation of the thin selective layer in the supported membrane was achieved by casting 1-wt% chitosan solution with and without fullereneol (1% to the weight of the polymer) onto the surface of the UPM and PAN supports and drying at room temperature to form a selective layer with a thickness of  $2 \pm 0.3$  μm, as determined by scanning electron microscopy. Cross-linking of the selective layer was achieved by heating the membrane to 140 °C for 100 minutes.

The maximum concentration of fullereneol was limited to 1 wt.% in the case of chitosan and 2 wt.% in the case of PPO because fullereneol concentrations exceeding these concentrations resulted in a poor dispersion of fullereneol in solution.

### 2.3. Preparation of PPO and PPO-fullereneol membranes

**2.3.1. Preparation of composites.** PPO-fullerenol composites containing 2 wt.% fullerenol were obtained by thorough mixing of PPO and fullerenol powders in agate mortar. After the solid-phase interaction the composites were dissolved in chloroform. The PPO/fullerenol solution was intensely stirred and sonified before membranes preparation.

**2.3.2. Preparation of membranes.** Dense membranes based on PPO and composites PPO-fullerenol with the thickness  $\sim 50 \mu\text{m}$  were obtained by casting a 4 wt.% polymer solution on a cellophane surface. The solvent was removed by evaporation at  $40^\circ\text{C}$ ; the membranes were separated from the substrate and dried in a vacuum oven at  $40^\circ\text{C}$  up to the constant weight

Supported membranes were prepared by casting 4 wt.% PPO (or PPO-fullerenol) solutions in chloroform on the surface of an MFFC support consisting of a fluoroplast F42L layer and polypropylene base. To create a selective layer with  $6\text{--}8 \mu\text{m}$  thickness. Then, the composite membrane was dried at room temperature during 1 day and after in a vacuum oven at  $40^\circ\text{C}$  up to constant weight.

#### 2.4. Scanning electron microscopy

SEM micrographs of the fracture surfaces perpendicular to the membrane plane were obtained using a Zeiss Merlin SEM. The homogeneous membranes were submerged in liquid nitrogen for five minutes and fractured perpendicular to the surface. The prepared specimens were observed using SEM at 1 kV.

#### 2.5. Pervaporation experiments

The transport properties were studied using a laboratory cell [5].

A downstream pressure of  $< 10^{-2}$  kPa was maintained using a vacuum pump and was controlled by a pressure gauge. The permeate was collected in a liquid nitrogen trap, weighed, and then analyzed via gas chromatography. The gas chromatograph used (SHIMADZU GC-2010) was equipped with a HP-PLOT/U column and a thermal conductivity detector to perform a quantitative analysis of the feed and the permeate composition.

The membrane permeation flux  $J$  ( $\text{kg}/\text{m}^2\text{h}$ ) was determined to be the amount of liquid transported through a unit of the membrane area per hour and was calculated as:

$$J = \frac{W}{A \times t} \quad (1)$$

where  $W$  (kg) is the weight of the liquids that permeated through the membrane,  $A$  ( $\text{m}^2$ ) is the effective membrane area, and  $t$  (h) is the measurement time.

Each measurement was performed at least three times, and the average value was recorded for later analysis.

#### 2.6. Swelling Study

Two types of dry non-porous membranes from PPO and chitosan were immersed in liquid at  $20^\circ\text{C}$  and atmospheric pressure for 10 days. At definite intervals, the swollen membranes were taken out from the weighing bottles, carefully wiped with filter papers to remove residue liquid on the membrane surface, and then quickly weighed. The experiment was carried out until the swollen membranes obtained a constant weight that indicated a state of sorption equilibrium. Then, the membranes were placed in a vacuum box at  $40^\circ\text{C}$  for 7 days to control the weight of the dry membranes. The liquids under the study depend of the studied polymer and were water, THF, and ethanol. The degree of the swelling was calculated by the following equation:

$$S_w = \frac{M_s - M_d}{M_d} \quad (2)$$

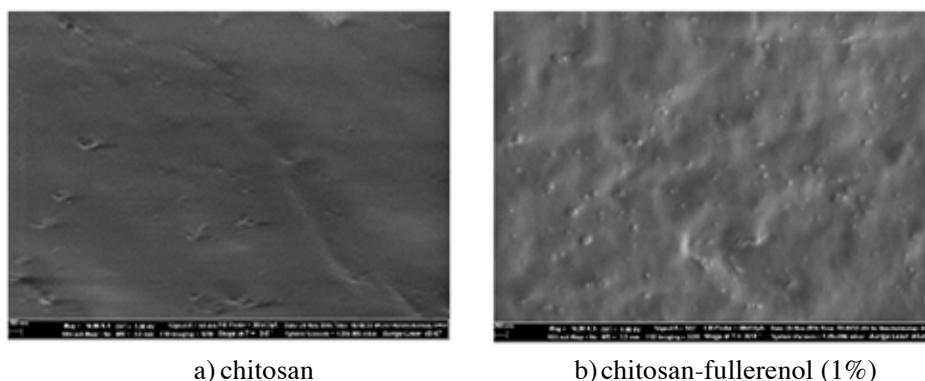
where  $M_s$  is the weight of a swollen membrane in equilibrium state and  $M_d$  is the weight of a dry membrane.

### 3. Results and discussion

#### 3.1. Scanning electron microscopy

A detailed study of the inner membrane structure was carried out by scanning electron microscopy (SEM) using the Zeiss Merlin SEM microscope.

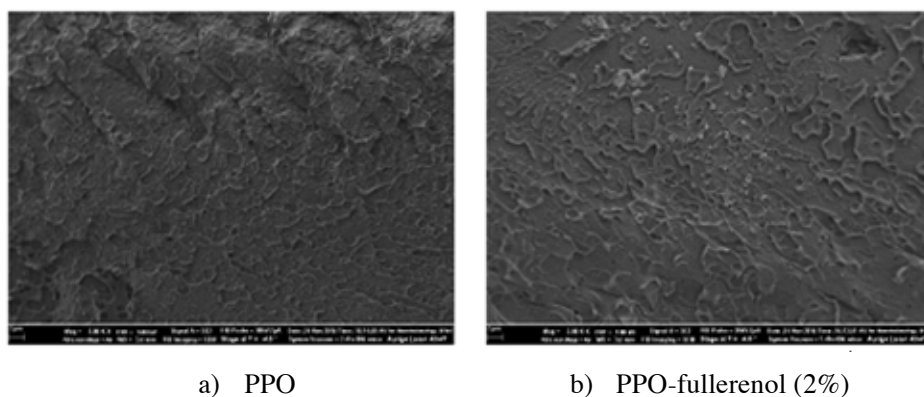
Figure 1 shows micrographs of the membrane cross-sections showing the features of the internal structure of chitosan-based membranes and the chitosan-fullerenol composite containing 1 wt.%  $C_{60}(OH)_{12}$ .



**Figure 1.** SEM micrographs of the cross-section of heat-treated membranes (140 °C 100 minutes) based on: a) chitosan, b) chitosan-fullerenol (1%)

For membranes based on chitosan and its composite with fullerenol (Figure 1), the following changes are observed: cross-section of a membrane from pure polymer is relatively homogeneous, while for a membrane with 1 wt.% fullerenol surface roughness is observed and inclusions of nanoparticles are visible.

Figure 2 shows micrographs of dense membranes based on PPO and PPO-fullerenol (2 wt.%) composite. As can be seen from the figure 2, the membrane from pure PPO has a roughness structure and heterogeneity, which increases with the introduction of fullerenol into the polymer matrix.



**Figure 2.** SEM micrographs of cross-section of membranes based on:  
a) PPO, b) PPO-fullerenol (2%)

The presented SEM micrographs demonstrated that the properties of the polymer matrix depend not only on the method of film formation, but also on the filler, in this case fullerenol. These changes in morphology under modification of the membranes with fullerenol are directly reflected on other physico-chemical and transport parameters of the membranes, the results of which are presented in next sections.

### 3.2. Sorption data

The study of the equilibrium swelling of polymeric membranes was carried out for two reasons, the first is the determination of the degree of cross-linking of polymer chains (for chitosan). For this study, the membranes were immersed in water. The second reason is that the first stage of the pervaporation mechanism is sorption, so there is a need to study the sorption characteristics of the membranes with respect to the components of the separated mixtures (ethanol, tetrahydrofuran (THF)) to explain the mechanism of transport of low molecular substances through the membrane. The results are shown in Table 1.

**Table 1.** Sorption characteristics of dense membranes.

Membrane	Sorption, %		
	THF	Ethanol	Water
chitosan	0,4		354,1
chitosan-fullerenol (1%)	0		330,3
PPO		7,8	0
PPO-fullerenol (2%)		4,1	0

The results presented in Table 1 indicate a decrease in the sorption capacity of fullerenol-modified membranes with respect to solvents as compared to unmodified membranes. The data of the table demonstrate that the degree of swelling in water and tetrahydrofuran of membranes based on chitosan decreases with the introduction of fullerenol into the polymer matrix, which indicates the cross-linking of polymer chains. Water is practically not sorbed by membranes from PPO and PPO-C<sub>60</sub>(OH)<sub>12</sub>. While the introduction of fullerenol into the PPO matrix reduces the degree of swelling in ethanol to 4.1%. Thus, the obtained data demonstrate different sorption behavior of membranes, which directly affects their transport characteristic. In the case of chitosan, the very low degree of swelling in THF and, conversely, the very high degree of water sorption indicate that both sorption and diffusion phenomena will favor water transport. On the other hand for PPO, the selective transport is expected to arise mainly from the facilitated diffusion of water in the glassy network.

### 3.3. Pervaporation data

The study of the transport properties of membrane was carried out in the process of pervaporation, which is an actual membrane process for the separation of low-molecular substances, especially for azeotropic, close-boiling and difficult-to-separate mixtures that are difficult to separate by simple separation methods. For the evaluation of membrane materials for industrial scale applications, it is necessary to take into account such properties as the possibility of using a membrane to separate the feed mixture and creating a supported membrane with a thin selective layer to increase productivity. The investigation of dense membranes is necessary to analyze the transport characteristics of the selected polymer and to exclude the influence of the substrate and defects in the selective layer of the supported membranes. The creation of composite supported membranes allows a significant increase in permeability.

*3.3.1 Transport properties of membranes based on chitosan and chitosan-fullerenol composite. Pervaporation of tetrahydrofuran (THF) - water mixture.* The transport properties of membranes based on chitosan and its composite with fullerenol have been studied by separating the azeotropic composition of a mixture THF-water at 20°C by pervaporation. Tetrahydrofuran is an important universal aprotic solvent. In the production process, water is a by-product of the reaction, in connection with which its dehydration is necessary. The difficulty in separating the THF-water mixture is that the THF forms an azeotropic mixture with water (5.7 wt.% water), which has a boiling point of 63.4°C, as well as strong hydrogen bonds. Thus, the use of distillation to separate this system is not advisable.

**Table 2.** Pervaporation of a mixture THF-water azeotropic composition at 20°C using dense and supported membranes based on chitosan and chitosan-fullerenol composite.

	Membranes (140°C 100 min)	Flux (kg/m <sup>2</sup> h)	Permeate, wt. %	
			water	ethanol
<b>dense</b>	chitosan	0.090	97.35	2.65
	chitosan-fullerenol (1%)	0.063	99.34	0.66
<b>supported</b>	chitosan /UPM	0.133	94.05	5.95
	chitosan /PAN	0.125	96.38	3.62
	chitosan-fullerenol (1%)/PAN	0.099	98.37	1.63

Table 2 shows the transport properties for thermally cross-linked (140°C 100 minutes) dense and supported membranes based on chitosan and chitosan-fullerenol(1%) composite. Dense membranes were studied to explain the mechanism of mass transfer. However, for use in industry, the thickness of the membrane must be reduced that can be achieved by creating supported membranes by depositing a thin selective layer on a porous support. In this paper, industrial ultrafiltration membranes based on polysulfonamide (UPM) and polyacrylonitrile (PAN) were chosen as porous supports. The thickness of supported membranes was about 2 µm. The flux for supported membranes increased in 1.47 times for the membrane on the UPM support and 1.38 fold for the PAN compared to the chitosan-based dense membrane. However, for the supported membrane on the UPM the selectivity with respect to water was decreased (to 94 wt.% of water) in the permeate compared to the dense membrane (97.35 wt.%) while the supported membrane on the PAN has good level of selectivity (96.38 wt.% water in permeate). Thus, the membrane on the PAN support was selected for further modification with a nanoparticle and further study. The introduction of 1 wt.% fullerenol into the chitosan matrix of the supported membrane on PAN significantly increased the selectivity (up to 98.37 wt.% water in the permeate) with a relatively similar flux (Table 2). Thus, a new effective nanocomposite supported membrane for purifying THF from water impurities was obtained.

*3.3.2 Transport properties of membranes based on PPO and PPO-fullerenol composite.* Pervaporation of a mixture of ethanol-water. The effect of fullerenol C<sub>60</sub>(OH)<sub>12</sub> (2 wt.%) on the transport properties of PPO membranes was studied for the separation of water-ethanol mixture. This mixture was chosen as previous studies demonstrated that for ethanol-water mixtures PPO exhibits water selective properties. In this case the modification of PPO by fullerenol could lead to the improvement of transport characteristics due to the change of surface and inner morphology of the PPO membranes. The system under investigation is characterized by azeotropic composition point: 95.57 wt.% ethanol and 4.43 wt.% water at 20°C, 760 mmHg. The obtained results are presented in the table 3.



**Table 3.** Pervaporation of a mixture ethanol-water with azeotropic composition at 20°C using dense and supported membranes based on PPO and PPO-fullerenol composite

	Membranes	Flux (kg/m <sup>2</sup> h)	Permeate, wt. %	
			water	ethanol
dense	PPO	0.014	92.98	7.02
	PPO-fullerenol (2%)	0.028	95.12	4.88
supported	PPO /MFFC	0.181	91.41	8.59
	PPO-fullerenol (2%)/MFFC	0.313	94.11	5.89

It was found that the introduction of fullerenol into the PPO matrix increases the flux (up to 0.028 kg / m<sup>2</sup>h) and the membrane selectivity (up to 95.12 wt.% water in the permeate) when the azeotropic point of the ethanol-water mixture was separated. The high selective properties established for the PPO-fullerenol(2%) membrane make it promising for participation in real ethanol purification processes. However, the investigated membrane has a significant disadvantage - low productivity, which is largely determined by the thickness of the membrane. The dense membranes based on PPO had a thickness of ~ 50 µm. To increase flux and preserve the mechanical characteristics, supported membranes consisting of a thin selective layer based on PPO and PPO-fullerenol(2%) composite (~ 2 µm) were deposited on a porous substrate that provided mechanical strength and practically no resistance to penetrant transport. The industrial MFFC membrane based on a copolymer of vinylidene fluoride and tetrafluoroethylene (fluoroplastic F42L) on a polypropylene base was used as the support. The choice of this type of support provided, above all, high flux and slightly changed of the separation factor. Thus, the creation of a supported membrane based on the PPO-fullerenol(2%) composite leads to a significant increase in flux (up to 0.313 kg/m<sup>2</sup>h) with comparatively the same selectivity (94.1 wt.% of water in the permeate) compared with the dense PPO-fullerenol(2%) membrane, which indicates the creation of a highly effective membrane for the purification of ethanol from water.

#### 4. Conclusions

Novel dense mixed-matrix membranes based on chitosan and PPO were developed using low-hydroxylated fullerenol C<sub>60</sub>(OH)<sub>12</sub> as selective nanoparticles. In the case of chitosan, fullerenol acts also as a crosslinker. The introduction of fullerenol into the two different polymer matrices favors to rise the transport of water and creation of dehydration membranes with improved pervaporation transport properties. Clearly the use of fullerenol as nano-modifier for chitosan and PPO membrane led to the increase both flux and selectivity. The application of fullerenol as cross-linking for chitosan caused the increase of selectivity with the similar level of flux. Supported membranes having a thin, dense layer were also successfully prepared. These membranes exhibited much higher fluxes – factor 15 to 20 – while keeping almost constant the water selectivity.

#### 5. References

- [1] Sudareva N N, Penkova A V, Kostereva T A, Polotskii A E and Polotskaya G A 2012 Properties of casting solutions and ultrafiltration membranes based on fullerene-polyamide nanocomposites *Express Polym. Lett.* **6** 178–88
- [2] Penkova A, Toikka A, Kostereva T, Sudareva N and Polotskaya G 2008 Structure and Transport Properties of Fullerene–Polyamide Membranes *Fullerenes, Nanotub. Carbon Nanostructures* **16** 666–9
- [3] Penkova A V., Acquah S F A, Sokolova M P, Dmitrenko M E and Toikka A M 2015 Polyvinyl

- alcohol membranes modified by low-hydroxylated fullereneol C<sub>60</sub>(OH)<sub>12</sub> *J. Memb. Sci.* **491** 22–7
- [4] Penkova A V., Acquah S F A, Dmitrenko M E, Sokolova M P, Mikhailova M E, Polyakov E S, Ermakov S S, Markelov D A and Roizard D 2016 Improvement of pervaporation PVA membranes by the controlled incorporation of fullereneol nanoparticles *Mater. Des.* **96** 416–23
- [5] Penkova A V., Acquah S F A, Dmitrenko M E, Chen B, Semenov K N and Kroto H W 2014 Transport properties of cross-linked fullereneol–PVA membranes *Carbon N. Y.* **76** 446–50
- [6] Uragami T, Matsuda T, Okuno H and Miyata T 1994 Structure of chemically modified chitosan membranes and their characteristics of permeation and separation of aqueous ethanol solutions *J. Memb. Sci.* **88** 243–51
- [7] Uragami T, Kato S and Miyata T 1997 Structure of N-alkyl chitosan membranes on water-permselectivity for aqueous ethanol solutions *J. Memb. Sci.* **124** 203–11
- [8] Ghazali M, Nawawi M and Huang R Y M 1997 Pervaporation dehydration of isopropanol with chitosan membranes *J. Memb. Sci.* **124** 53–62
- [9] Volkov V I, Skirda V D, Vasina E N, Korotchkova S A, Ohya H and Soontarapa K 1998 Self-diffusion of water-ethanol mixture in chitosan membranes obtained by pulsed-field gradient nuclear magnetic resonance technique *J. Memb. Sci.* **138** 221–5
- [10] Ren J and Jiang C 1998 Transport Phenomena of Chitosan Membrane in Pervaporation of Water-Ethanol Mixture *Sep. Sci. Technol.* **33** 517–35
- [11] Qunhui G, Ohya H and Negishi Y 1995 Investigation of the permselectivity of chitosan membrane used in pervaporation separation II. Influences of temperature and membrane thickness *J. Memb. Sci.* **98**
- [12] Shih C-Y, Chen S-H, Liou R-M, Lai J-Y and Chang J-S 2007 Pervaporation separation of water/ethanol mixture by poly(phenylene oxide) and sulfonated poly(phenylene oxide) membranes *J. Appl. Polym. Sci.* **105** 1566–74
- [13] Khulbe K C, Matsuura T, Lamarche G and Kim H J 1997 The morphology characterisation and performance of dense PPO membranes for gas separation *J. Memb. Sci.* **135** 211–23
- [14] Polotskaya G A, Penkova A V, Toikka A M, Pientka Z, Brozova L and Bleha M 2007 Transport of small molecules through polyphenylene oxide membranes modified by fullerene *Sep. Sci. Technol.* **42** 333–47