

Modification of Glass-Fibre Reinforced Polyester Plastics with 2,4-Toluene Diisocyanate During Moulding

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Summary

The exotherms and mechanical strength changes due to different amount of 2,4-toluenediisocyanate in glass-fibre reinforced polyesters are considered. It is found that the higher the concentration of 2,4-toluenediisocyanate (i) the shorter the gelation time (ii) the faster the polymerization during gelation and (iii) the greater the exothermic effect of the process. As a whole, the reinforcement effect of the glass-fibre composites is bigger than that of non-reinforced polyester. Tensile, bending and impact strength improvements for reinforced polyesters are in the range of 15-25, 27-38 and 21-32 %, respectively in comparison with 12 % for the same tests of non-reinforced one. The data received reveal the opportunity for an effective modification of such plastic articles during the process of their formation. The reached impact resistance is comparable with those ones for some standard SMC (sheet moulding compound) materials. The tensile strength of 85 MPa (at 120°C) is commensurable with and even higher than that one of many advanced polymeric materials tested at ambient temperature.

Keywords:

unsaturated polyester resins; glass-fibres-reinforced polyesters; toluene diisocyanate modification; cold press moulding

Introduction

It is well known [1] that introducing of small quantities of isocyanates changes the curing mechanism of some sheet moulding products (type ITP – SMC material and technology of Union Carbide). Multifunctional compounds synthesized by interactions of isocyanates with hydroxyl-containing acrylic and fumaric oligomers are reported [2-4]. High-viscous or hard intermediate products were obtained in both cases. They were further transformed into articles by moulding at high temperature and pressure. The modification of glass-fibre reinforced polyesters with 2,4-toluene diisocyanate is considered in a previous report [5]. The choice of a modifier and some attending effects are discussed too. The present research is a continuation of this study. The basic idea now is to unite the processes of the glass-fibers' impregnation

with resin and copolymerization of the styrene with the unsaturated oligoesters as well as their interaction with the isocyanate modifier in one process, done at low pressure and temperature. Improved mechanical properties of the glass fiber reinforced plastics are expected. An additional result of this work is the clarifying of a possible way to make better the ecologically harmless low-pressure technologies for direct moulding processing of glass fiber reinforced plastic articles with relatively small quantity of glass fibres such as resin transfer moulding (RTM), 'cold press moulding' and laminating sheet methods. That is why the results are of scientific and practical interest.

Experimental section

1. *Materials and reagents*

1.1. Unsaturated polyester resin – "Vinalkyd 550PE" (a commercial product of "Orgachim" Ltd., Rouse) contains 65% unsaturated oligoesters (mol. weight about 800) and 35% styrene.

1.2. Cyclohexanone peroxide (CHPO) – "Peroximon K4" (a commercial product of ATO ELF Atochem), as hardener, is 50% solution in phthalate plasticizer.

1.3. Cobalt octoate (CoOt_2) – "Accelerator NZ495" (a commercial product of AKZO), as accelerator, is 1% Co^{2+} concentration in phthalate solvent.

1.4. 2,4-Toluene diisocyanate (TDI) – "Desmodur T80" (a commercial product of Bayer) contains 80% 2,4-toluene diisocyanate and 20% 2,6-toluene diisocyanate.

1.5. Glass-fibre mat made of 'E'-glass – "TM-5057 12264". This is a commercial product of Ahlström – 450 g/m^2 randomly oriented fibers (length of about 60mm and tex 1200) with not readily soluble binder resin (500 sec. in styrene).

2. *Preparation of samples for mechanical testing*

The glass fiber reinforced plastic plates with 4 ± 1 mm thickness were made by the 'cold press moulding' method. They were reinforced with 4 or 5 layers of glass fiber mat. The unsaturated polyester resin was initiated with 2 wt.% CHPO and 1 wt.% CoOt_2 . The moulding was done by means of a hydraulic press in circumstances as follows: pressing rate – up to 10 mm/min; pressure 0.3 MPa; initial temperature 25 °C and moulding duration from 10 to 45 min according to the composition. The glass fibres content in the plates was 33 wt.% or 40 wt.% for 4 and 5 glass fiber mat layers respectively.

3. *Methods for mechanical measurements*

3.1. The tensile strength (10 samples) was accomplished according to ASTM D638 (ISO 527) using a standard "Instron-1185" testing machine. (Instron Ltd., England).

3.2. The bending strength (10 samples) was determined according to ISO-178 using the same machine.

3.3. The impact resistance (12 samples) without notch was determined according to DIN 53453 (ISO 179) using 'CEAST 6548/000' (CEAST S.p.A., Italy).

4. Investigation of polymerization kinetics of the unsaturated polyester resin

50 \pm 0.1 g of initiated unsaturated polyester resin was poured in a heat-insulated vessel. The temperature was measured by thermocouple and was registered by electron recording device. A standard automatic timer for gelation time recording was used. The initial temperature of the unsaturated polyester resin was 25 °C.

Results and discussion

The introduction of TDI in the unsaturated polyester resin shortens the gelation time and overall technological duration due to distinct increase of polymerization rate (fig.1):

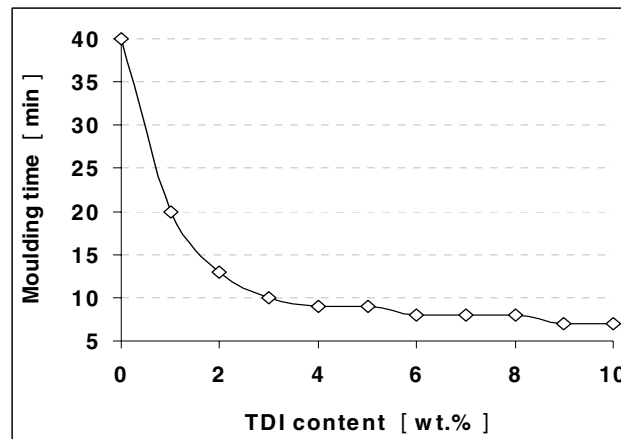


Figure 1. Moulding time vs. the content of TDI in unsaturated polyester resin in case of 'cold press moulding' technology (4 layers of glass fiber mat - 33 wt.%; initiating system: 2 wt.% CHPO and 1 wt.% CoOt₂, in relation to the unsaturated polyester resin)

From the technological point of view, very fast gelation will lead to worse impregnation of the glass-fibre reinforcement and low final mechanical strength. That is why the information about the polymerization kinetics of the unsaturated polyester resin containing different TDI concentrations is so important.

The resin was initiated with 1.5wt% CHPO and 1wt% CoOt₂ for an experimental purpose. The used quantity of TDI was introduced in the unsaturated polyester resin first, followed by CoOt₂ and then the mixture was intensively stirred. After 3-4 min. the CHPO was added. The mixture was stirred briefly but thoroughly again, poured in the heat-insulated vessel and thermally examined (fig.2).

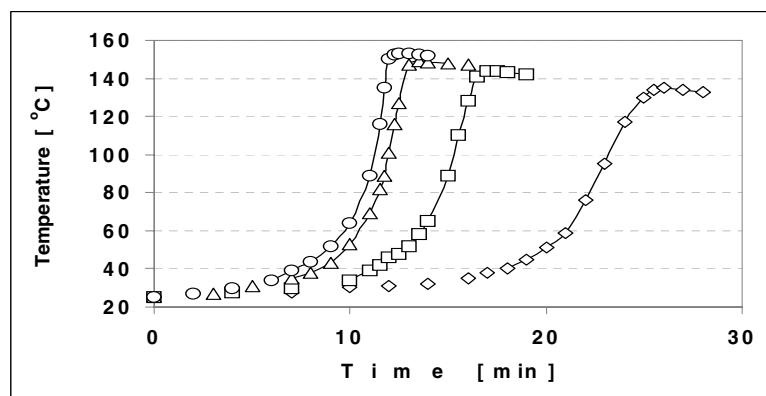
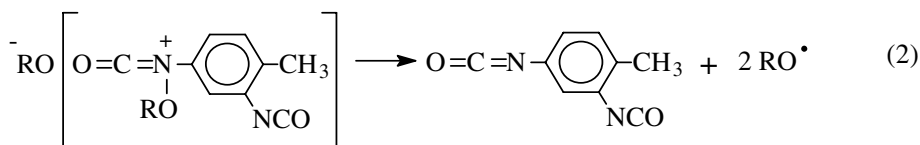
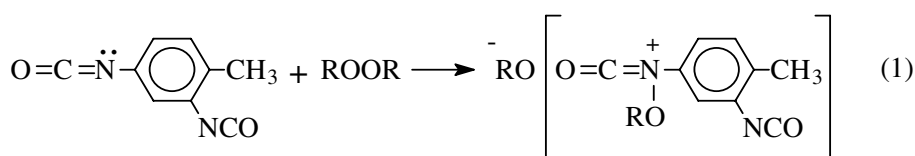


Figure 2. Dependence of the exotherm and gelation time on the amount of TDI in unsaturated polyester resin (TDI concentration: \diamond - 0 wt.%; \square - 2 wt.%; Δ - 5 wt.%; \odot - 8 wt.%)

The exothermic effect is sufficient so to reveal clearly the TDI influence on the unsaturated polyester resin polymerization kinetics. It is easy to see that the higher the concentration of TDI (i) the shorter the gelation time (ii) the faster the polymerization rate during gelation and (iii) the greater its exothermic effect.

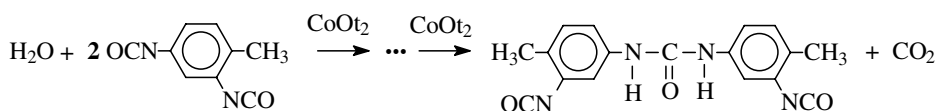
There are two main reasons for the acceleration of the unsaturated polyester resin polymerization in the presence of TDI. The first is the catalytic action of the isocyanate groups on the peroxide decomposition and the second one is the simultaneous deactivation of the inhibitor (hydroquinone).

The nitrogen atom in the isocyanate group possesses an unshared electron pair by which, like aromatic tertiary amines, it forms an unstable complex with the peroxide initiator. So, the decomposition rate to radicals takes place much quicker than that of the peroxide only:



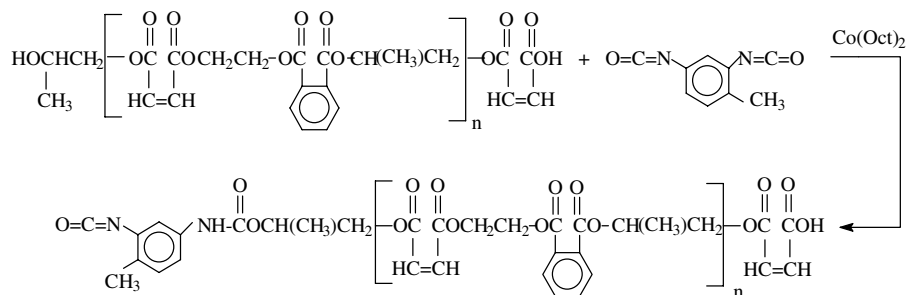
The isocyanate reacts easily with the hydroxyl groups of hydroquinone. In our case, TDI eliminates the possibility for classical interactions between the hydroquinone and the peroxide or the polyester macroradicals. The final effect is acceleration of the unsaturated polyester resin polymerization and hence the glass-fibre reinforced plastic processing. So, in case of the “cold press moulding” method the process shortens several times. Additional effect could be realized for the ecologically harmless “direct technologies”. Due to the moulding in closed instruments, the negative oxygen influence, as an inhibitor, is excluded and the resin curing accelerates still further.

An additional advantage of the TDI is its capability to react easily with water :



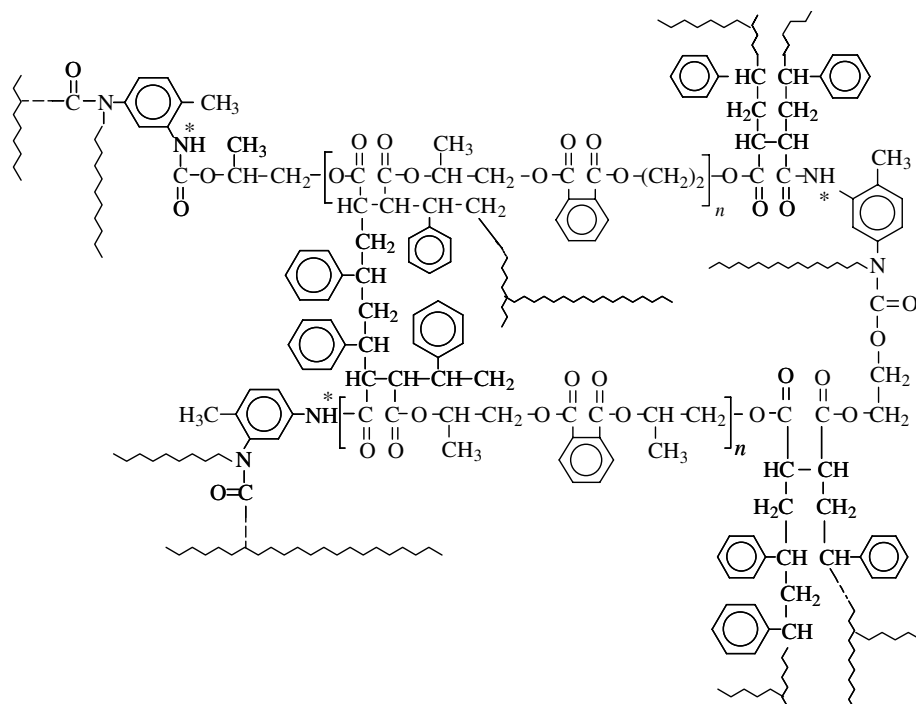
The water is introduced by glass reinforcing materials or accumulates as a by-product during the reactions in the media.

After the mixing of the unsaturated polyester resin with TDI, at relatively low temperature, the hydroxyl groups of the unsaturated oligoesters react predominantly with the *p*-isocyanate groups of 2,4-TDI [6]. The reaction is stimulated by the presence of CoOt_2 [7] :



This process coincides with the induction period of the free-radical copolymerization between the styrene and the unsaturated polyester oligomer. As the reaction is exothermic, the temperature increases depending on the TDI concentration (Fig.2). When the temperature reaches 80-90 °C, the *o*-isocyanate groups of TDI are activated too and they also react with the free hydroxyl and carboxyl groups. Thus, polyurethane bridges between the oligoester chains occur and aromatic imine groups form. They are active enough so as to react with other *p*-isocyanate group. So, a new cross-linking center is generated and a new junction is built. The net density is depending on the TDI concentration.

Model scheme of a fragment of the spatially cross-linked modified polyester matrix:



The model scheme of a fragment of the spatially cross-linked polymer matrix presents a variant of bonding through urethane and imide bonds. The generation of acylurethane, biuret and aliphant bonds are also possible [8].

According to the thermodynamic of adhesion [9], there are four reasons for improvement of the mechanical properties of the glass fiber reinforced plastics modified with TDI:

- the improved wetting and hence the increased adhesion between the glass fibers and the unsaturated polyester resin;
- the increased adhesion work due to strengthening of the polymer phase and the surface tension;
- the elimination of water and glycols (remained from the unsaturated polyester resin synthesis) from the interface surface by their inclusion in the polymer structure;
- the formation of the stronger chemical bond between TDI and non-silanized hydroxyl group from the glass phase than intermolecular interaction.

That is why the next part of our investigation reveals some changes in the mechanical strength of these composites.

In order to establish the influence of the modification with TDI on the mechanical properties of the glass fiber reinforced plastics containing orthophthalate polyester matrix, series of suitable samples have been examined.

The first test (fig.3) concerns tensile strength changes as a function of TDI content in the composite.

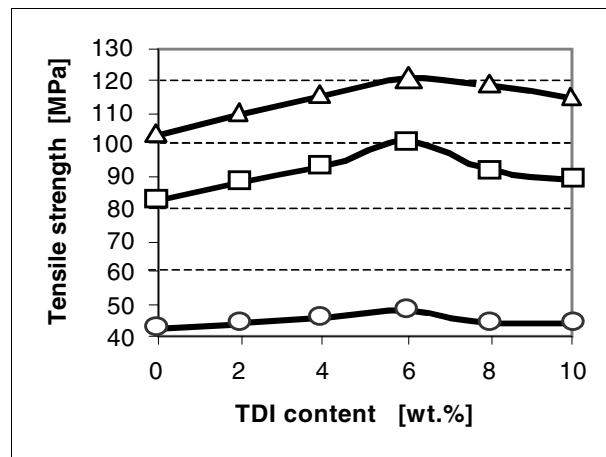


Figure 3. Tensile strength vs. the content of TDI in polyesters (○-unsaturated polyester resin, □-the glass fiber reinforcement is at about 33 wt.%, △- the glass fiber reinforcement is at about 40 wt.%)

A passing glance on the slopes of the curves presented in Fig.3, reveals the better effect of the TDI modification upon the glass fiber reinforced plastics than the not reinforced ones. The differences can be explained with the additional improvement of the adhesion between the polymer matrix and the glass-fiber phase. A quantitative estimation notes the strengthening of about 15-25 % for glass fiber reinforced plastics comparing to 12 % for the not reinforced.

The second important feature of any composite on a fiber base is its ability to sustain bending forces. The data received in this relation are presented on fig.4.

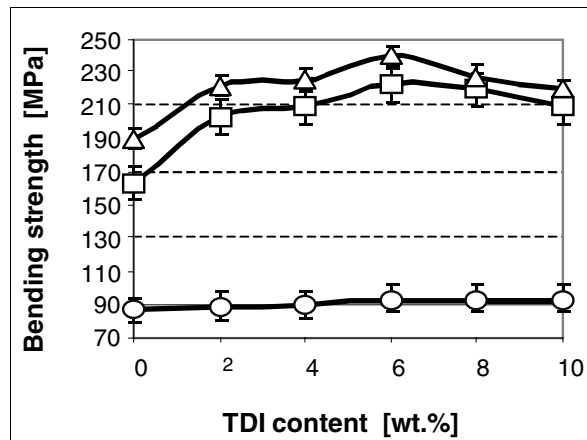


Figure 4. Bending strength vs. the content of TDI in polyesters (○-unsaturated polyester resin, □- reinforced with 33 wt.% glass fibres, △- reinforced with 40 wt.% glass fibres)

As it was expected, analogical behavior of tested samples were observed. It is important to note that the relative strengthening effect now is better than at tensile examination. Thus, for glass fiber reinforced plastics, it is about 27 % -38 % in comparison with 12 % for the not reinforced ones. Another similarity in both tests is that the maximum strength value is reached at 6 wt.% TDI content in the resin.

These results are very useful for the practice because such strength can be compared with those of other plastics reinforced with higher amount of glass fibers or produced by expensive technologies.

An important advantage of glass fiber reinforced composites is their resistance to impact loading. That is why the impact testing method is used to measure and compare these properties. The data thus obtained are illustrated on fig.5 :

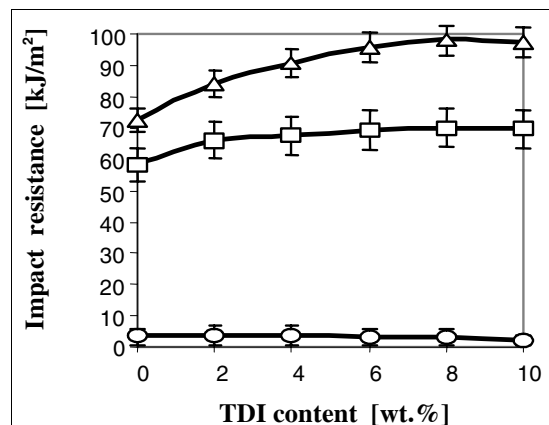


Figure 5. Impact resistance vs. the content of TDI in glass fiber reinforced plastics (○-unsaturated polyester resin, □-resin reinforced with 33 wt.% glass fibres; △- resin reinforced with 40 wt.% glass fibres)

As it can be easily seen the usage of TDI causes similar and significant change in curve trends of glass fiber reinforced samples.

The enhanced TDI content in the matrix of not reinforced material monotonically leads to product with higher rigidity and worse impact resistance. The behavior of the glass fiber reinforced plastics is opposite. The maximum relative strengthening effect is in the range of 21-32 %. The absolute values reached now are comparable with those ones for some standard SMC-materials. The highest strength is reached at TDI content of 8-10 wt.%. This means that the optimum strength will be a compromise due to lack of advantages for tensile and bending strength at these TDI concentrations.

The heat resistance of material could be a relative measure for the degree of cross-linking and strengthening of the adhesion interaction between the phases in polymer composite. That is why an investigation on the tensile strength at 120 °C of the both, not reinforced and glass fiber reinforced plastics with different amount of TDI, has been carried out (fig.6).

The increase of the TDI concentration above 4 wt.% leads to a better effect on the tensile strength. The recorded value of 85 MPa (at 120°C) is excellent. It is commensurable with, and even higher than, that ones of many advanced polymeric materials tested at ambient temperature.

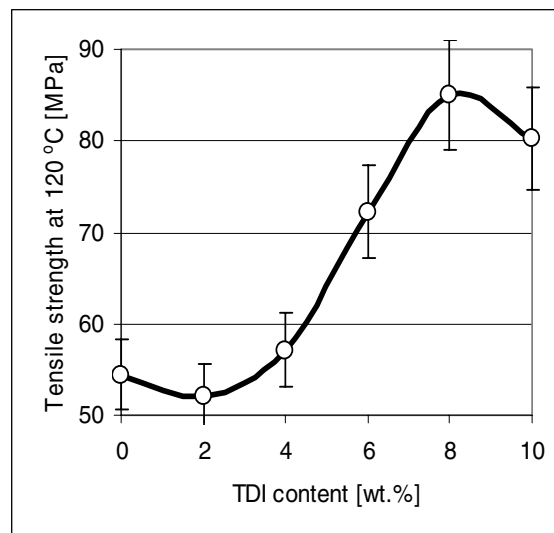


Figure 6. Tensile strength vs. the content of TDI in glass-fibre reinforced plastics at 120 °C (five glass-fibre mat layers - 40 wt.%)

Conclusions

1. The kinetic and mechanical investigations considered above reveal the opportunity for an effective modification with TDI of glass fiber reinforced plastic articles during the process of their formation using ecologically harmless, low-pressure technologies.
2. The modification with TDI speeds up several times the hardening process of the composites with polyester matrix and this way contributes to the intensification of the technologies of their production.

3. Higher TDI concentrations could be used for production of articles with middle and small overall dimensions.
4. For production of articles with greater overall dimensions, especially in the case of resin transfer moulding methods, the usage of TDI modified resins is possible too, if the number of the injecting pipes is increased and their disposition is optimized.
5. TDI modification improves the mechanical properties of the articles due to the better adhesion between the modified polymer phase and the reinforcement in the composite. The increase of the strength characteristics is also a function of the thickening of the polymer matrix as a result of the formation of interpenetrating polyester and polyurethane networks with common oligoesters links.

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References

1. Meyer RM (1990). Reinforced plastics thermoset matched molding, Handbook of plastic materials and Technology, New York., 989.
2. Spirin YL, Goudzera SS, Magdinetz VV, Krijanovska G (1974). Synthesis and applications of liquid oligomers containing urethane for preparing of reinforced polymeric materials., Rep Acad Sci USSR, 216, No3. 577:581.
3. Goudzera, SS., Spirin YL, Magdinetz VV, G.V.Krijanovska (1975). Influence of nature of the unsaturated component on the properties of oligourethane acrylates. Synthesis and physical chemistry of polymers, Moscow, No15, 132:136.
4. Goudzera, SS, Spirin YL, Magdinetz VV, Roudko AR (1976). Copolymerization of oligourethane acrylates with methylmethacrylate and styrene. *Synthesis and physical chemistry of polymers*. Moscow, No18, 13:20.
5. Radenkov M, Topliyska Ant, Marinova At, Radenkov Ph (2000). Modification of glass fiber reinforced polyesters with toluene diisocyanate. Symposium of reports of IX International Conference of Mechanics and Technology of composites, Sofia'2000, 254:258.
6. Kirpichnikov PA, Averko-Antonovich LA, Averko-Antonovich YO (1975). Chemistry and technology of the synthetic rubber. Leningrad, 'Chimia', 445:452.
7. Lee LI (1980). Rubber Chem. Technol. Vol. 153 (3).
8. Sigmund Orchon (1990). Polyurethanes, Thermoset. in: I. Rubin ed., Handbook of plastic materials and technology, 515:523.
9. Radenkov Ph, Radenkov M, Grancharov G, Troev K (2003), Direct usage of products of poly(ethylene terephthalate) glycolysis for manufacturing of glass-fiber-reinforced plastics, European Polym J, 39, 1223:1228.
10. Lypatov, YS (1986), Physical chemistry of multi-component polymeric systems, Vol.2, Kijv, Naukovaya dumka, 112:148.