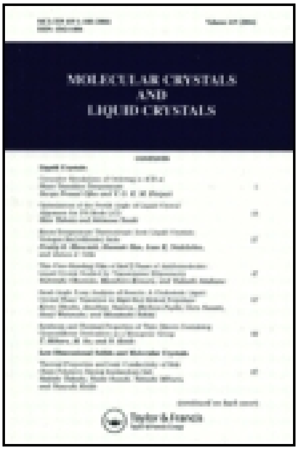

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Some New Directions of Development of Polymers and Plastics

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Some New Directions of Development of Polymers and Plastics

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Three new possibilities of obtaining resins and plastics are shortly signalised. New liquid anhydrous reactive solvents (RSs) have been obtained from different compounds containing active hydrogen atoms and formaldehyde have been obtained. These RSs dissolve monomers condensating with formaldehyde, especially melamine (Mel) and urea into anhydrous solutions, liquid at temperature of dissolving, containing up to 100 % of polymerising substances and up to 70 % Mel. At temperature of dissolving these solutions can be fast formed and cured, combining synthesis with processing of polymers in the common process of reactive forming. They can be used for fast bonding of natural fibers.

Plastified PVC crosslinks with aliphatic amines under gelling conditions into synthetic poromeric leatherlike materials with hygienic properties of natural leather and 30–40 % water vapour sorption and desorption.

It was found out that new ecological polyurethanes can be obtained from vegetable oil, urea and formaldehyde

Keywords: reactive solvents; condensation plastics; melamine; crosslinked poly(vinyl chloride); polyurethanes; vegetable oil

EXPERIMENTAL

Reactive Solvents of Monomers Condensating with Formaldehyde and Plastics Obtained from them

We have discovered a new class of anhydrous or almost anhydrous reactive solvents (RS), containing 90 – 100 % of active, polymerisable substances, liquid at room temperature or not higher than 333 K, dissolving monomers capable of polycondensating with formaldehyde, such as: urea, phenol, and especially the hardest of them to dissolve - melamine (Mel) and their derivatives[1-7]. After the dissolution of these monomers in our RSs at temp.333-433 K, we have obtained in a few minutes, first - liquid, anhydrous solutions and then resins, containing up to 100 % polymerisable substances and up to 70 % Mel or urea which can be formed and cured at once in a few minutes or so without a necessity of drying or distilling volatiles off. This is a new method of fast obtaining anhydrous condensation resins and plastics directly from monomers, similarly to the method of reactive forming of polyurethanes.

RSs are products of reaction with formaldehyde of compounds containing active hydrogen atoms C-H, N-H or O-H, called „skeleton compounds" (SC) onto their hydroxymethyl derivatives, their hemiformals and others (Fig. 1).

FIGURE 1 Fundamental reactions of obtaining of Reactive Solvents

1. $R\text{-}XH + CH_2O \rightarrow RXCH_2OH$
   $RXCH_2OH + n\,CH_2O \rightarrow RXCH_2O(CH_2O)_nH$
   $X = C\text{-}H$ (activ), O-H, N-H
2. $R\text{-}YH_2 + 2\,CH_2O \rightarrow R\text{-}Y(CH_2OH)_2$
   $R\text{-}Y\,(CH_2OH)_2 + 2\,CH_2O \rightarrow R\text{-}Y\,(CH_2OCH_2OH)_2$
   $Y = \text{-}NH_2, \text{-}CH_2\text{-}$
3. $R\text{-}CH_3 + 3\,CH_2O \rightarrow R\text{-}C(CH_2OH)_3$
   $R\text{-}C(CH_2OH)_3 + 3\,n\,CH_2O \rightarrow R\text{-}C(CH_2OCH_2OH)_3$

As SC containing active C-H groups ketones have been used, especially the cheapest of them - acetone, also cyclohexanone, acetaldehyde, nitromethane and lutidine (Table 1). As SC containing active O-H groups alcohols have been used, especially methanol. As SC containing N-H groups urea and Mel have been used (Fig.2).

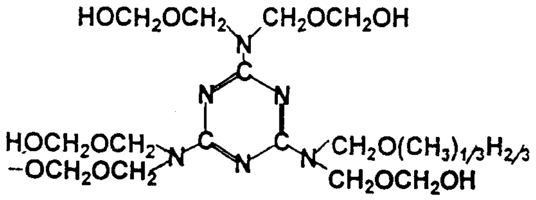
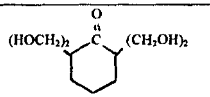
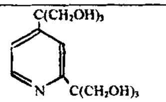


FIGURE 2 Molecule of reactive solvent MelF12 (common formula)

Table 1 Comparison of maximal temperature of dissolution and solubility of melamine in various reactive solvents

Reactive solvent	Chemical formula	Temperature of dissolution K	Solubility of melamine, % in solution
Tri(hydroxymethyl)acetaldehyde	$CHOC(CH_2OH)_3$	413	< 17
Mono(hydroxymethyl)acetone	$CH_3COCH_2CH_2OH$	413	14
Tris(hydroxymethyl)acetone	$CH_3COC(CH_2OH)_3$	413-423 373-383	40-60 14
Hexa(hydroxymethyl)acetone	$(HOCH_2)_3CCOC(CH_2OH)_3$	418	48
Reaction product of 1 M acetone with 8 M formaldehyde	$H(OCH_2)_2CH_2COC(CH_2OCH_2OH)_3$	373-383	48-50
Reaction product of 1 M acetone with 12 M formaldehyde	$CO[C(CH_2OCH_2OH)_3]_2$	373-383	56
Tetra(hydroxymethyl)cyclohexanone		413	50-62
Tris(hydroxymethyl)nitromethane	$O_2C(CH_2OH)_3$	403	46
Hexa(hydroxymethyl)lutidine		413	50

In this way we can obtain solutions of urea in RS from urea and solutions of Mel in RS from Mel, obtaining unmodified or optionally modified urea- or melamine-formaldehyde resins respectively, not containing any volatiles. Melting points (m.p.) of RSs should be not higher than 353 K, because at this temperature hemiformal groups irreversibly decompose, liberating free formaldehyde. M.p.of RSs depend on m.p. of SC and the number of formaldehyde molecules bonded with SC . When SCs are relatively low-polar such as acetone or methanol then m.p. of RSs rise with the number of formaldehyde molecules bonded with one molecule of SC. When SC are high polar as in the case of Mel or urea, then melting point of RSs decrease with increasing amount of CH_2O bonded into a molecule.

Viscosity of RSs increases with their melting point. Low viscosity of reaction mixture (r.m.) at dissolving temperature of Mel enables intensive mixing and then faster dissolving of Mel.

Mel first dissolves physically in RS, then formaldehyde splits off from RS

$$\text{-CO-C-(CH}_2\text{O)}_n\text{H} \rightarrow \text{-CO-C-(CH}_2\text{O)}_{n-1} + \text{CH}_2\text{O}$$

and reacts with Mel: $-NH_2 + CH_2O \rightarrow -NHCH_2OH$

then hydroxymethyl groups of Mel react with hydroxymethyl groups of RS (etherification): $\text{-N-CH}_2\text{OH} + \text{-C-CH}_2\text{OH} \rightarrow \text{-N-CH}_2\text{-O-CH}_2\text{-C-} + \text{H}_2\text{O}$

also with Mel itself (the fastest) reaction:

$\text{-N-CH}_2\text{OH} + \text{-NH}_2 \rightarrow \text{-N-CH}_2\text{-NH-} + \text{H}_2\text{O}$

forming Mel resin

The obtained resin, at temperature close to that of Mel dissolving, can cure very fast onto plastics. Solubility of Mel in RS is higher:

-the higher is temperature (figure 3),

-the faster rices the temperature of reaction mixture,

-the smaller are particles of melamine,

-the faster is mixing and

-the higher is water content in the reaction mixture.

The use of liquid, anhydrous solutions of condensation monomers in RSs will result in making a breaktrough in Mel and urea resins and plastics synthesis and processing.

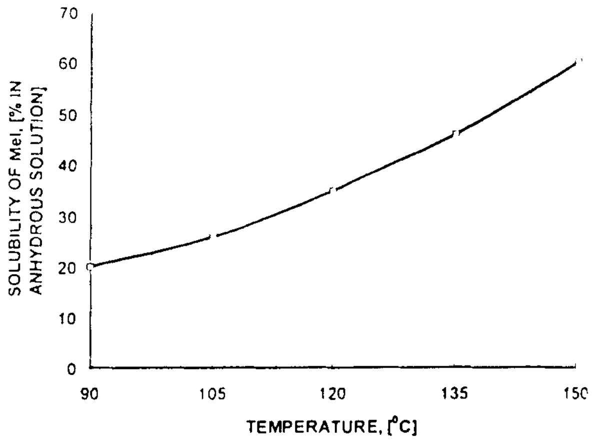


FIGURE 3 Dependence of solubility of melamine in tris(hydroxymethyl)acetone on temperature

The process of drying is eliminated from condensation plastics production. The necessity of separate obtaining of resin (e.g. in special factories) is also eliminated. The synthesis of polymers from raw materials can be combined with processing in one short process of reactive forming (Fig.4).

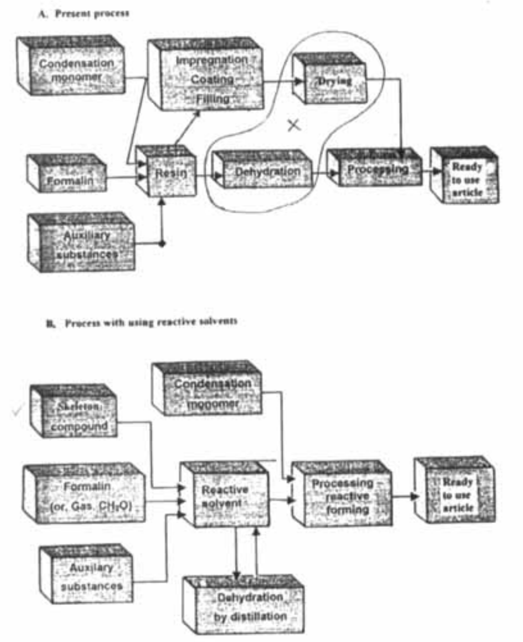


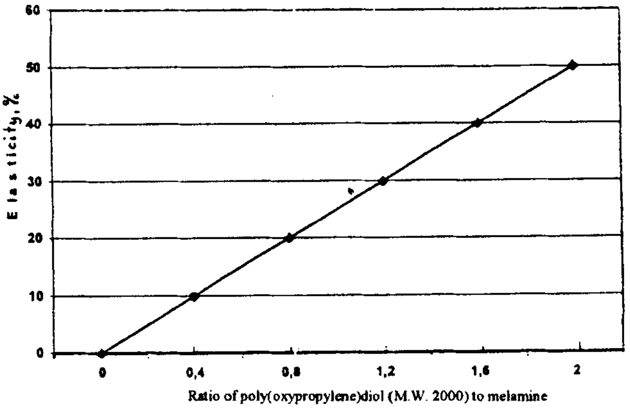
FIGURE 4 Diagram of production process of condensation formaldehyde plastics

This creates a possibility of producing ready plastics products in a few minutes, as well as construction materials (e.g.chipboards) from natural cellulosic fibers, bonded with anhydrous urea or melamine solutions in RSs. Waste cellulosic materials or annual plant straw can be also bonded with these solutions. Anhydrous solution of condensation monomers (CM) in RSs can be very quickly modified, and/or foamed with chemical foamers and cured to foams, ready to use without drying.

First, from solutions of Mel in multi(hydroxymethyl)acetone, we have obtained intumescent foams with closed cells, with apparent density of 20–100 kg/m^3 and thermal stability up to 473-573 K [6,7]. These foams are resistant to heat flux of 30 kW/m^2. At 573 K melamine foams become carbonized to black foams with smaller apparent density and higher thermal and mechanical strength than noncarbonized ones.

Melamine foams from Mel solutions in RSs, when sufficiently cured, do not emit perceptible amounts of formaldehyde

We have also obtained: foams from solutions of urea in AFn RS with apparent density up to 7 kg/m^3 and self-extinguishing hard to soft foams from PUR containing built in solutions of Mel in RS as a part of rigid segments of PUR, in the place of more expensive isocyanate (fig.5). Compression strength these PUR-Mel foams is higher than that of the unmodified ones (Fig.6).



- Elasticity = % of reduction thickness of foam sample under pressure without cracking of polymer

FIGURE 5 Dependence of elasticity of PURM foam from solution of melamine (1 w.p. in 1.67 w.p. of 87 % aqueous solution RS AF3) on the amount of poly(oxypropylene)diol (PP-2000) with M.W. 2000

Foamed solutions of CMs in RSs can be used also for bonding light chip boards or other fibrous materials.

The solution of Mel in RS AF8 has been used now for production of decorative laminates. By butoxylation with butanol of anhydrous solutions of Mel in RSs Mel coating resins have been obtaied very fast.

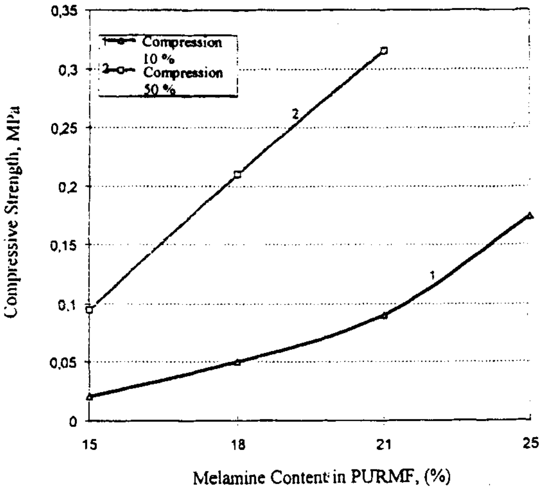


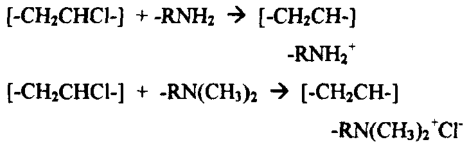
FIGURE 6 The PURMF compressive strength vs. melamine content in the PURMF

High solubility of Mel (or urea) in RS (up to 75 % of Mel in solution) creates a possibility of obtaining polymer with molar ratio of CH_2O : Mel (or urea) as low as 1:1. In this way it is possible to obtain also linear polymers, which can not be obtained by routine reaction of Mel with formalin in aqueous solution, because in the latter melamine or urea resins should have hydroxymethyl groups,ensuring them solubility in water. Linear polymer without hydroxymethyl groups will not split free CH_2O during exploitation. However, to get considerable advantages from using solutions of CMs in RSs, the production installation has to be adapted for this purpose.

2. Plastified Crosslinked Poly(Vinyl Chloride) for Higienic Leatherlike Materials [8-11]

Plastified poly(vinyl chloride) (PVC) is a cheap polymer used for obtaining nonhygienic, coated, leatherlike materials, i.e. for clothing and shoes production. Main disadvantages of these materials are both impermeability to water vapour and very low water vapour sorption and desorption. Therefore our work was aimed at obtaining stable, opencapillary poromeric films of crosslinked PVC, plastified with dioctylphtalate (DOP), possibly with encreased water vapour sorption and desorption (SaD), as a raw material for the production of cheap, hygienic leatherlike materials (LLM). Such materials have not been produced in the world until now. We have found that PVC can be crosslinked with hardly volatile primary (and tertiary) aliphatic di- and tri-amines during gelation of its pastes with DOP in temperature range of 408-443 K, about 40-60 K lower than gelling temperature of PVC without amines. A crosslinked, plasticized polymer is flexible and does not dissolve in typical (even hot) PVC solvents (i.e. cyclohexanone, dimethylformamide). From crosslinked, plasticized PVC film only the plasticizer is extracted by solvents.

Amine groups react with PVC substituting chlorine atoms in the polymer chains. HCl splitted from PVC in this reaction of condensation is bonded by amine group which has been added to polymer chain .



$$[\text{-}CH_2CHCl\text{-}] + \text{-}RNH_2 \rightarrow \underset{\text{-}RNH_2^+}{[\text{-}CH_2CH\text{-}]}$$

$$[\text{-}CH_2CHCl\text{-}] + \text{-}RN(CH_3)_2 \rightarrow \underset{\text{-}RN(CH_3)_2^+Cl^-}{[\text{-}CH_2CH\text{-}]}$$

Amine crosslinked PVC contains ion pairs, making it hydrophilic. It has been found, that crosslinked plasticized PVC has SaD of water vapour above 10 %, i.e. much higher than noncrosslinked one (0.5-1.0 %), reaching in some cases up to 30%, which corresponds to SaD range of natural leather (10-50 %). Plasticized crosslinked PVC behaves like an elastomer and has elastic memory. If PVC-dissolving, water miscible, unsensitive to amine action solvent is added to the paste before gelation and then washed out with water from crosslinked polymer, then a stable open-capillary poromeric structure is formed in the place of solvent. Under electron microscope, a fine capillary structure of polymer was found with of capillaries below 1 μm in diameter. Net of capillaries under the surface is connected with their outlets on the surface of polymer (Fig.7). This structure is steady because crosslinking of polymer prevents its flowing. 50 % of PVC crosslinking is enough for stabilization of capillary structure. The film of polymer was obtained with 50 –10 % of crosslinking and up to 42 % of porosity. In this way the two most important higienic properties of leatherlike materials were achieved: water vapour SaD and poromeric structure

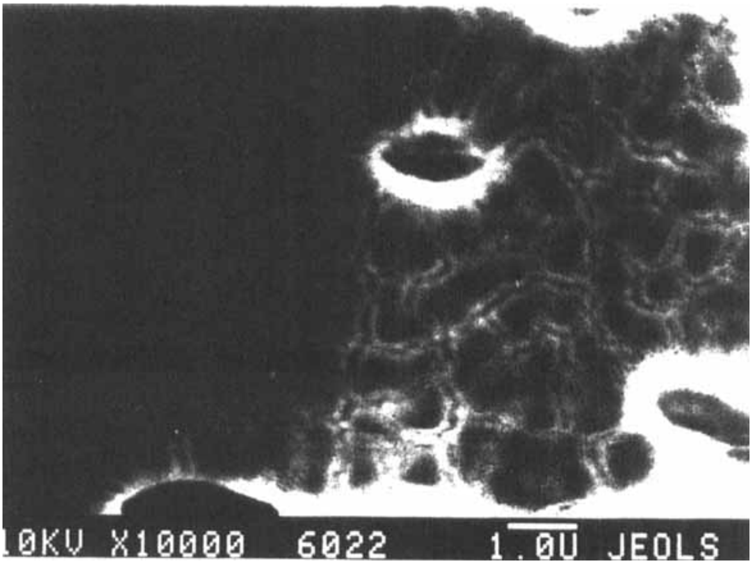


FIGURE 7 Electron Micrograph of Surface of Poromeric, Crosslinked, Plastified PVC with Net of Capillaries , Magnification 10000x.

About 20 hard volatile aliphatic and aliphatic-aromatic primary and tertiary di- and tri-amines and their derivatives were obtained (some of them for the first time) and used as crosslinkers for PVC.

. The efficiency of PVC crosslinking was the highest at the temperature of 408-418 K for primary amines and about 453 K for tertiary amines. The highest water vapour SaD was observed in the case of PVC films crosslinked with a mixture of CLEDA (reaction product caprolactame with ethylenediamine) and N-ethylaminacetamide (N-EAAA), with valeramide N,N-bis(diethylamine) (VADETA), with ethylene,bis(oxyethylene)-1,10-diamine (TEDA) and their adducts with carbon dioxide.

TABLE 2 Some amines used for modification and crosslinking of PVC

$CH_3CONHCH_2CH_2NH_2$	N-EAAA
$C_4H_9CON(CH_2CH_2NH_2)_2$	VADETA
$H_2N(CH_2CH_2O)_2CH_2CH_2NH_2$	TEDA
$H_2N(CH_2)_5CONHCH_2CH_2NHCO(CH_2)_5NH_2$	CLEDA
$H_3^+NCH_2CH_2NHCH_2CH_2NHCOO^-$	adduct DETA with CO_2

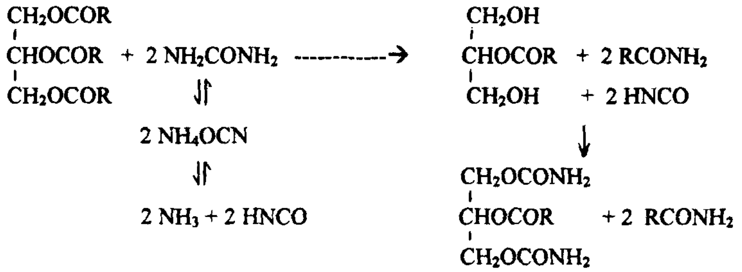
The permeability of water vapour through poromeric films reached the value of 36 g/(m^2· h. 0.1 mm). The water vapour permeability is the higher the higher is the porosity of crosslinked films . Tensile strength of the crosslinked films was of the same order as that of non-crosslinked ones. An important advantage of crosslinking PVC with amines is the fact that amines immediately react with unsaturated bonds. Thus, even if PVC contains traces of carcinogenic vinyl chloride, the latter is quantatively eliminated (bonded by amine) from polymer during the production of leatherlike material.

If plasticized PVC crosslinked with adducts of aliphatic amines with CO_2 is foamed, the product obtained is characterised by water vapour SaD up to 30-40 %.and its dimension increase with water vapour sorption and decrease with desorption like natural leather.

Hygienic leatherlike materials obtained from crosslinked, plasticized, poromeric PVC, characterized by water vapour sorption, desorption and permeability , similar to natural leather are expected to find application as a new generation material in footwear and clothing industry. They will be cheaper than leather and polyurethanes as well as more higienic than PUR and noncrosslinked PVC.

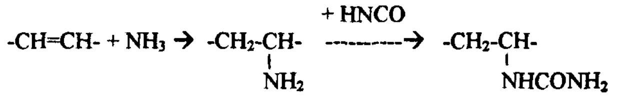
3. New Possibilities of Obtaining Ecological Monomers, Polymers and Plastics

It was found that urea reacts with vegatable oil at temperature of about 433 K in the heteregenous system almost quantatively (about 98.5 %). .The main reaction is amidolysis of oil to glyceride carbamates.



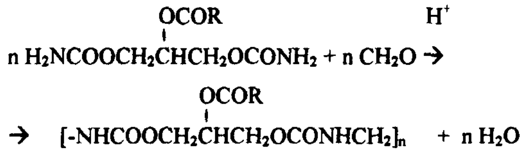
$$\begin{array}{lcl} CH_2OCOR & & CH_2OH \\ | & & | \\ CHOCOR + 2\,NH_2CONH_2 & \longrightarrow & CHOCOR + 2\,RCONH_2 \\ | \quad\quad\quad \downarrow\uparrow & & | \\ CH_2OCOR \quad 2\,NH_4OCN & & CH_2OH + 2\,HNCO \\ \quad\quad\quad \downarrow\uparrow & & \downarrow \\ \quad\quad\quad 2\,NH_3 + 2\,HNCO & & CH_2OCONH_2 \\ & & | \\ & & CHOCOR + 2\,RCONH_2 \\ & & | \\ & & CH_2OCONH_2 \end{array}$$

It was found that unsaturated bonds in fatty acids of oil react also first with ammonia and then with isocyanic acid into ureas. Monoglyceride dicarbamates and ureacarbamates are valuable raw materials for obtaining polyurethanes and polyurethaneureas and can also serve as modifiers of different *condensation resins and plastics (urea, melamine and phenol)* built in their composition and enhancing their hydrophobicity, elasticity and solubility in organic solvents.



$$-CH{=}CH- + NH_3 \rightarrow -CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}- \xrightarrow{+HNCO} -CH_2-\underset{\displaystyle NHCONH_2}{\underset{|}{CH}}-$$

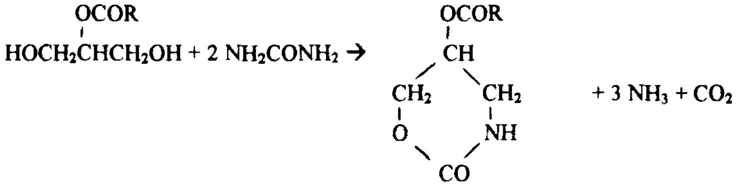
From monoglyceride dicarbamates and carbamateureas in reaction with formaldehyde, aliphatic ecological polyurethanes can be obtained e.g. :



$$n\,H_2NCOOCH_2\overset{\displaystyle OCOR}{\overset{|}{C}}HCH_2OCONH_2 + n\,CH_2O \xrightarrow{H^+}$$
$$\rightarrow [-NHCOOCH_2\overset{\displaystyle OCOR}{\overset{|}{C}}HCH_2OCONHCH_2]_n + n\,H_2O$$

Besides fatty acid amides created in the reaction process they are valuable raw materials for obtaining of auxilaries for processing of plastics.

From monoglycerides and urea at temerature of 348 K, cyclic urethane monoglycerides have been obtained. This cyclic urethane could be used for obtaining polyurethanes from vegetable oil by polymerisation or polyaddition.



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