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Developments in aqueous polyurethane and polyurethane-acrylic dispersion technology Part I. Polyurethane dispersions[*)]

Janusz Kozakiewicz[1), **)]

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Abstract: In this paper which is Part I of the review article concerning developments in aqueous polyurethane dispersions (APUD) and aqueous hybrid polyurethane-acrylic dispersions (APUAD) the current methods of APUD synthesis are reviewed and the developments in investigations of the effect of starting materials and process parameters on properties of dispersions and films are discussed based on recent literature data. The most important developments in the field of APUD and areas where further research may still be required are suggested.

Keywords: aqueous polyurethane dispersions, aqueous poly(urethane-urea) dispersions, ionomers, coatings, adhesives.

Postępy w technologii wodnych dyspersji poliuretanowych i poliuretanowo-akrylowych. Cz. I. Dyspersje poliuretanowe

Streszczenie: W Cz. I artykułu dotyczącego rozwoju technologii APUD (wodne dyspersje poliuretanowe) oraz APUAD (wodne dyspersje poliuretanowo-akrylowe) dokonano przeglądu stosowanych obecnie metod syntezy APUD i, na podstawie aktualnej literatury, przeprowadzono analizę postępów w badaniach wpływu rodzaju materiałów wyjściowych i parametrów procesu na właściwości wytwarza-

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[1)] Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland.

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[**)] Author for correspondence; e-mail: janusz.kozakiewicz@ichp.pl

nych dyspersji i powłok. Przedstawiono też najważniejsze osiągnięcia w dziedzinie APUD i wskazano obszary, w których jest konieczne przeprowadzenie dalszych badań.

Słowa kluczowe: wodne dyspersje poliuretanowe, wodne dyspersje poli(uretanowo-mocznikowe), jonomery, materiały powłokowe, kleje.

AQUEOUS POLYURETHANE DISPERSIONS AS A CLASS OF WATERBORNE POLYURETHANES

Due to specific structure (sequence of flexible polyol and hard isocyanate segments, high polarity and strong hydrogen bonding) as well as practically infinite possibilities for tailoring the structure to the needs of the formulator, polyurethanes[*)] exhibit certain specific features, including: *i.a.*, high mechanical strength combined with elasticity and chemical and abrasion resistance which make them widely used, mainly in the form of rigid or flexible foams, elastomers, coatings, adhesives and sealants. Introduction of hydrophilic groups either as chain segments or as pendant groups makes polyurethanes water-dispersible, usually without external surfactant. The term „waterborne polyurethanes" [1—3] covers a range of products comprising aqueous polyurethane dispersions (APUD) and aqueous polyurethane-acrylic dispersions (APUAD) [4, 5], water-reducible urethane alkyds [6], associative polyurethane thickeners [7, 8] or aqueous systems based on water-dispersible polyisocyanates and polyols [9, 10]. A number of books and reviews have been published dealing with waterborne polyurethanes — see *e.g.*, [1, 2, 9] and specifically with APUD and APUAD [11—15] which are the most widely recognized class of waterborne polyurethanes. The global demand for APUD and APUAD is currently around 300 000 tons per annum and is constantly growing at a rate *ca.* 5 % per year [16] due to introduction of restrictions on using organic solvents in coatings and similar products, specifically in Europe [17].

The standard, commercially available APUD is a semi-transparent or milky-white liquid having solids content of *ca.* 30—35 % and relatively low viscosity (normally *ca.* 100—300 mPa·s). It is worth to mention here that although commercially available APUD which have solids concentrations usually not exceeding 35 % are very stable, it was proved [18] that even slight increase in solids content over that value led to increased viscosity and — when the solids content was 40 %+ even to gel formation, especially when the dispersions were subjected to temperatures up to 70 °C. APUD usually form glossy and transparent films with hardness, elasticity and adhesion depending on chemical structure of the dispersed polymer. The characteristic feature of APUD is very small particle size (normally *ca.* 50—150 nm) and therefore they may be considered colloidal solutions.

This paper (Part I of the review) focuses on developments in synthesis, characterization and application of APUD, primarily over the last decade *i.e.*, after a most recent detailed review concerning synthesis, molecular structure, characterization and applications of polyurethanes, including APUD, was published [19] though certain earlier developments will also be emphasized. Very soon Part II of this review article will be published as a separate paper [20]. It will concern synthesis and characterization of APUAD, methods of crosslinking of films produced from APUD and APUAD, filled and two-component systems involving APUD and APUAD, and applications of those dispersions.

DEVELOPMENTS IN SYNTHESIS OF AQUEOUS POLYURETHANE DISPERSIONS

Methods of synthesis

Commercially available so called „aqueous polyurethane dispersions" are in fact aqueous dispersions of poly(urethane-urea) anionomers or cationomers. The most common schemes of reactions leading to those structures are shown in Scheme A and Scheme B, respectively.

The structure of final polymer of which fine particles of ionomer polyurethane dispersion are formed may look like that presented in Fig. 1 [21] which shows (1) phase separation involving hard urethane and urea segments and soft polyol segments that is characteristic feature of polyurethanes and (2) complex interactions between various moieties.

Synthesis of anionomer (also called „anionic") APUD (Scheme A) comprises reaction of polyol with diisocyanate in the presence of a diol holding acidic group (usually dimethylolpropionic acid — DMPA — is used), neutralizing the resulting urethane prepolymer terminated with NCO groups with tertiary amine and emulsifying the prepolymer-ionomer thus formed in water followed by reaction with polyamine or diamine. Such sequence of reactions leading to partly crosslinked or linear polymer containing ionic groups is commonly known as „prepolymer-ionomer" or „prepolymer mixing" process. Disadvantage of this process is a need to dilute the viscous prepolymer-ionomer with high-boiling co-solvent (usually *N*-methylpyrrolidone — NMP — is used for that purpose) before emulsifying it in water. However, other techniques are presently possible to diminish prepoly-

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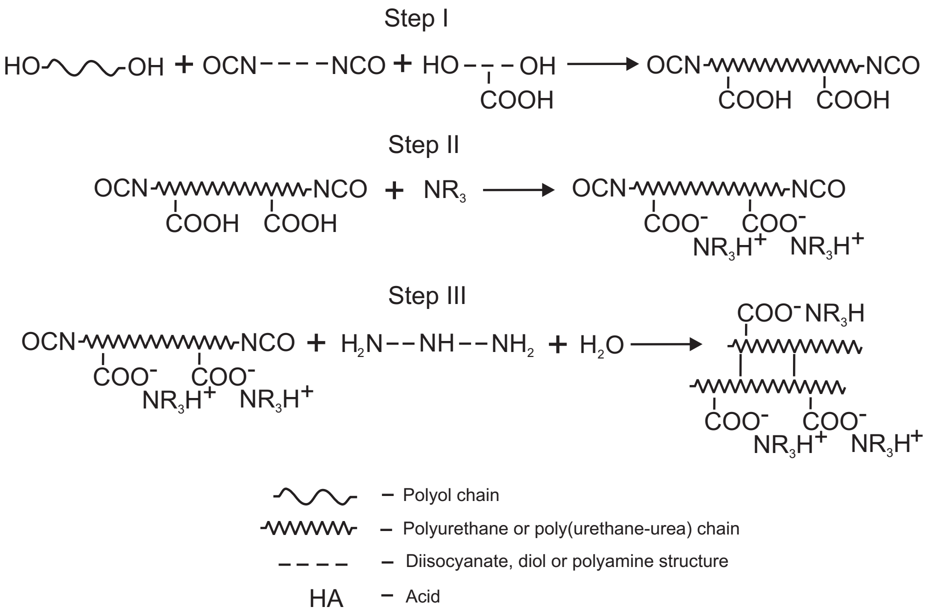
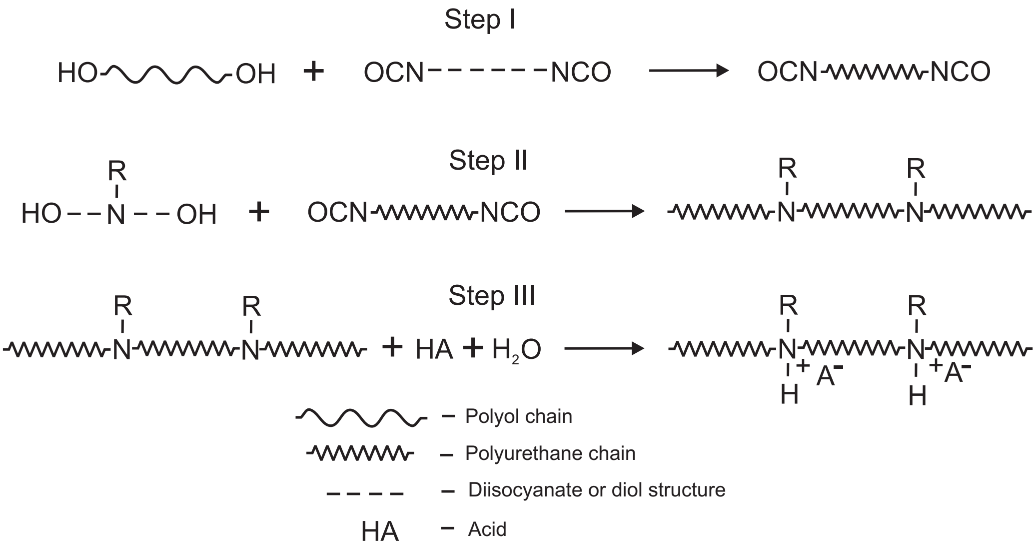
[*)] In a common sense the term „polyurethanes" is used not only for polyurethanes (which contain urethane group in the main chain), but also for polyureas (which contain urea group in the main chain) and poly(urethane-urea)s (which contain both urethane and urea groups in the main chain).



Scheme A



Scheme B

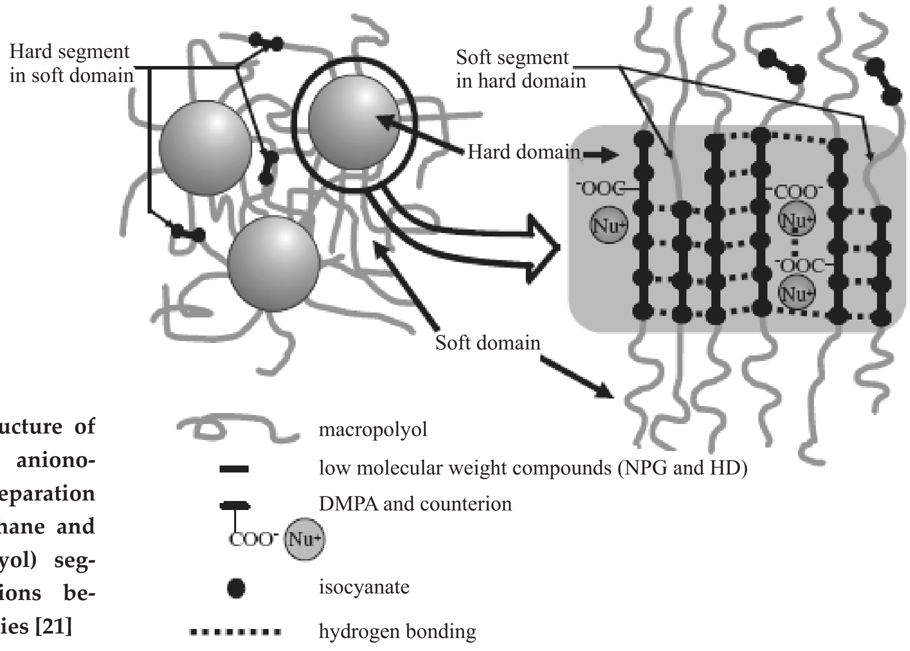


Fig. 1. Schematic structure of poly(urethane-urea) anionomer showing phase separation involving hard (urethane and urea) and soft (polyol) segments and interactions between different moieties [21]

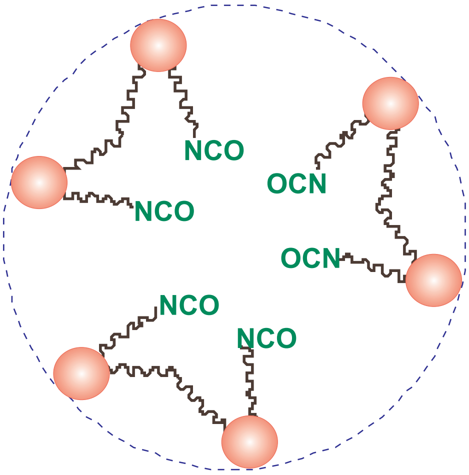


Fig. 2. Schematic representation of associated hydrophobic segments of the prepolymer-ionomer which protect NCO groups from contact with water: ● — ionic groups

mer-ionomer viscosity and produce solvent-free APUD — see further text for details. Though the prepolymer-ionomer is terminated with free NCO groups which, especially in the presence of tertiary amine, easily react with water, it can be effectively emulsified in water without gelling of the contents of the reactor because in water the hydrophobic parts of polymer chains associate, so that NCO groups are somehow protected (Fig. 2). Relatively slow reaction of free NCO with water in such aqueous systems was confirmed by the authors of a paper presented at Waterborne, High Solids and Powder Coatings Symposium in 1995 [22].

Addition of polyamine that is much more reactive with NCO than water results in partial crosslinking of prepolymer-ionomer chains. Since another process that may proceed in such system is neutralizing the COOH groups with polyamine (if neutralization of COOH groups with tertiary amine was not complete) or even replacing tertiary amine with polyamine, the molar ratio of tertiary amine to polyamine is of great importance — see Section "Effect of neutralizing and chain extending agent" for details.

Diols can be applied instead of di- or polyamines as chain extenders in the process of synthesis of anionomer APUD, but since diols react with NCO at roughly the same rate as water, it is usually recommended that the extension step is done before emulsifying of the prepolymer-ionomer in water even if catalyst which favors the NCO-OH reaction is applied. Moreover, if diols are applied as chain extenders one has to take into account the significant increase in viscosity of the system due to chain extension. The problem of viscosity increase can be resolved through applying so called „acetone" process for conducting the anionomer APUD synthesis. The „acetone" process is described briefly further down in this Section.

Synthesis of cationomer (also called „cationic") APUD comprises formation of NCO-terminated urethane prepolymer followed by chain extension with alcoholamine (usually *N*-methyl diethanolamine) used in nearly equimolar amount and quaternization of tertiary amine groups present in the main polymer chain with either acid or alkyl halide, and eventually emulsifying the resulting cationomer in water, usually containing some small amount of diamine that is able to react with any remaining NCO groups. Usually, in contrast to synthesis of anionomer dispersions described earlier, formation of dispersion of cationomer in water is achieved by addition of water to the cationomer. As the cationic groups of the cationomer may form ionic bonds with counter-anion that is introduced with acid (or produced in the process of quaternization using alkyl halide) ionic crosslinking may occur along with hydrogen bonding leading to high mechanical strength of films produced from cationomer dispersions [5]. Comparison of properties of cationomer and anionomer APUD and of films produced from them was presented in [23].

Though the commercially available APUD are currently usually produced via „prepolymer ionomer" processes described above, also other methods of APUD synthesis are known. First method to mention here is so called „acetone" process which actually was developed even before inventing the „prepolymer-ionomer" method [24], but later was partly abandoned due to high cost. The „acetone" process may be conducted using the same sequence of reactions as the „prepolymer ionomer" process so the solution of the prepolymer-ionomer in acetone is emulsified in water and reacted with polyamine and then acetone is removed (*e.g.*, distilled off) though other approaches are also possible. One of those approaches comprises using hydrophilic polyamine bearing ionic (*e.g.*, SO_3^-) groups as chain extender [3], so there is no neutralization step involved, and the other comprises conducting chain extension of prepolymer-ionomer with polyamine or diol [25, 26], still in acetone solution. In both approaches discussed above the final step of the process is diluting the resulting anionomer solution with water and removal of acetone (or other water-miscible low-boiling solvent) to produce aqueous dispersion. The phase inversion phenomenon that occurs during removal of acetone was studied in detail by the authors of [25].

Other methods of APUD synthesis are also described in the literature [27] which comprise (1) so called „ketamine" or „ketazine" process where a blocked polyamine (usually ketamine or ketazine, but also other blocked amines can be considered) is admixed with the prepolymer-ionomer, so only after dispersing in water immediate hydrolysis occurs and the released polyamine reacts with NCO groups and (2) so called „polymer melt" or „hot melt" process in which ammonia or urea is reacted with prepolymer-ionomer to obtain terminal urea or biuret groups, respectively, which are then methylolated with formaldehyde and the resulting polymer is dispersed in water. Though both alternative methods of anionomer APUD synthesis mentioned above have been known for quite a long time they have not been widely used, probably because APUD produced in ketimine or ketazine process will contain some amount of ketone released during hydrolysis, and APUD produced in hot melt process will contain residual formaldehyde.

Finally, APUD can be also synthesized in miniemulsion. In that process first reported in [28] diol, diisocyanate and a hydrocarbon solvent were emulsified in water and then the resulting emulsion was sonicated and heated up to speed-up the reaction. Obviously, NCO groups reacted both with diol and with water (side reaction), so actually poly(urethane-urea) was obtained, but by using dibutyltin dilaurate as catalyst the main reaction with diol was found to be predominant. Miniemulsion polymerization is also important route to obtain APUAD, but this process will be described in Part II of this review.

Effect of various factors on synthesis of anionomer APUD and on the properties of corresponding films and coatings

Effect of polyol and isocyanate

Undoubtedly, the properties of APUD and of films and coatings obtained from APUD depend primarily on type of polyol and diisocyanate used in synthesis of the urethane prepolymer and on their molar ratio that affects the prepolymer chain length as well as hard segments content in final polymer and consequently influences the properties of final polymer. In [29] the anionomer APUD were synthesized from two different diisocyanates (isophorone diisocyanate — IPDI and tetramethylxylilene diisocyanate — TMXDI) and two different polyols (polycaprolactone and polypropylene glycol) using fixed molar amounts of DMPA applied as component bearing COOH group and ethylenediamine applied as prepolymer-ionomer chain extender, and the effect of diisocyanate/polyol (NCO/OH) molar ratio on the properties of the resulting dispersions and films was investigated in detail. It was found that increase in NCO/OH ratio not only led to increase in glass transition temperature (T_g) of the soft phase of the poly(urethane-urea) ionomer film (what could actually be expected because the increase in urethane and urea groups content in the polymer chain resulted in increased physical crosslinking through hydrogen bonding), but also to increase in surface free energy (*SFE*) of the film surface (Fig. 3a and 3b, respectively).

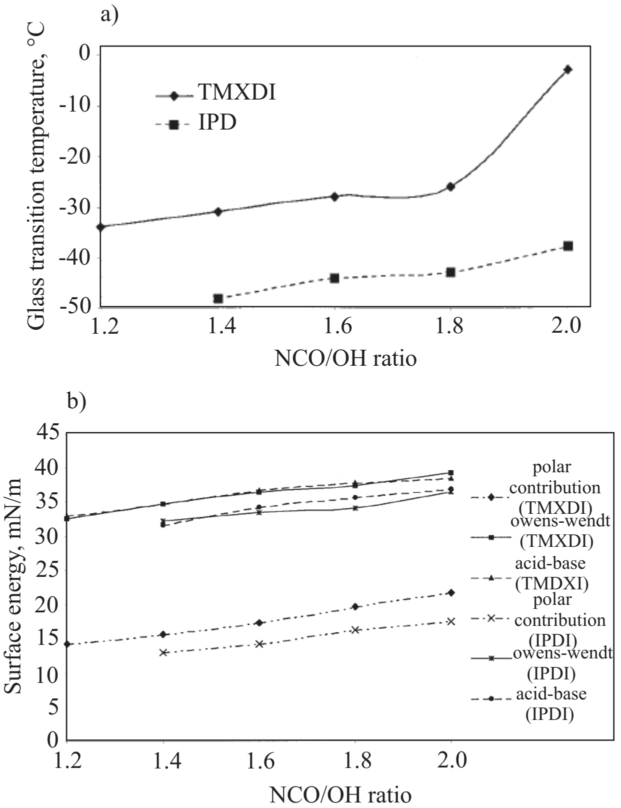


Fig. 3. Effect of NCO/OH ratio applied in synthesis of urethane prepolymer on properties of the film produced from APUD obtained from two different polyols: a) effect on T_g, b) effect on *SFE* [29]

The increase in surface free energy with increase in NCO/OH molar ratio could be explained by increase in polarity of the polymer. It is interesting that also average particle size of dispersions was affected by NCO/OH ratio — a significant decrease from 85 nm to 35 nm was observed with increase in NCO/OH from 1.2 to 2.0. This effect might be due to lower viscosity of prepolymer-ionomer synthesized using higher NCO/OH molar ratio, which allowed for formation of smaller dispersion particles during emulsifying of that prepolymer-ionomer in water, but according to the authors of that paper the reason could also be higher proportion of more hydrophilic urea groups which could act as internal emulsifier. However, the investigations carried out by other authors using another set of starting materials for prepolymer-ionomer synthesis [30] showed that particle size increased when fraction of hard segments (corresponding to NCO/OH molar ratio) increased and it was explained by the fact that with increasing hard segment fraction the polymer chain became harder and the formation of polymer micelles in water needed more chains to stabilize the micelle structure. Similar results were obtained in the more recent studies [31, 32], but increasing dispersion particle size with increase in molar NCO/OH ratio was explained by lowering the amount of ionic moieties per polymer molecule in the same time. This explanation can be supported by the fact that decrease in ionic groups content in the polymer leads to increase in dispersion particle size (see Section "Effect of hydrophilic group"). Apparent differences in the results of the studies on the effect of NCO/OH on dispersion particle size and in interpretation of those results clearly show that more research is needed in that respect, specifically taking into account that the mechanism of micelle formation (which in the case of APUD is quite complex) has not yet been studied in detail since the pioneer work on synthesis and characterization of APUD was published [24].

NCO/OH molar ratio was also seriously affecting the mechanical properties of films prepared from anionomer APUD obtained from prepolymer-ionomers synthesized from mixtures of hydroxyl-terminated polybutadiene (HTPB) with polypropylene glycol, DMPA and IPDI. Lower NCO/OH ratio resulted in higher mechanical strength of the films [33]. The same effect was observed in a more recent study [32] where APUD were obtained using polycaprolactone as main polyol component and TMXDI as diisocyanate and NCO/OH molar ratio of 1.4—1.6 was found to be the most suitable for application of such dispersions as wood coatings.

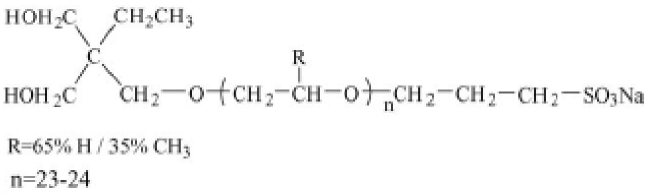
The influence of structure and type of polyol on properties of APUD and films was studied in detail, too [34]. It was found that the polyol structure significantly affected stability and average particle size of dispersions as well as soft phase T_g and *SFE* of films. Polypropylene glycol was claimed to be the most suitable polyol for dispersion synthesis in terms of low prepolymer-ionomer viscosity and low dispersion particle size. Important role of polyol chain length was also proved.

Apart from the most common polyester polyols like poly(ethylene adipate) or polyether polyols (like polytetramethylene glycol or polypropylene glycol) also polyols with some specific structure are used as main components for synthesis of APUD. Good example is using a phosphated polyol as starting material for APUD recommended as binder for corrosion-protecting coatings [35] However, special attention has been given by the researchers to the use of polyols originating from natural resources as starting materials for APUD. Castor oil was most frequently used as starting polyol for APUD synthesis since it contains hydroxyl groups. Anionomer APUD were successfully synthesized from castor oil, IPDI and DMPA via „acetone" process, but using methyl-ethyl ketone instead of acetone [36]. In that paper a detailed discussion of the effect of various factors on rheological properties and gelling behavior of the resulting APUD was presented and the results of investigations of morphology of dispersion particles were also reported. In another study, saturated polyester diol derived by transesterification of castor oil with a waste obtained in glycolysis of poly(ethylene terephthalate) was applied as main component in synthesis of anionomer APUD [37]. Similarly, cationomer APUD was synthesized from methoxylated soybean-oil polyols [38]. Findings from a detailed study on synthesis and characterization of APUD based on natural oils (castor oil and soybean oil) which contains a comprehensive list of the relevant references were reported in [39]. Recently, two novel approaches to castor oil-based APUD were reported. One was synthesis of APUD containing polyurethane-aromatic polyamide sulfone copolymer which was prepared by using amino-terminated polyamide sulfone as chain extending agent for prepolymer-ionomer synthesized from castor oil [40]. Another was synthesis of „fully bio-based" APUD using castor oil and a diisocyanate produced from undecylenic acid derived from castor oil as the main starting materials [41].

Polycarbonate diols have been often selected as starting materials for commercially available APUD applied for wood lacquers since they provide the highest coating hardness as well as good elasticity at low temperatures and resistance to oils [42, 43]. While standard polycarbonate diols are synthesized using 1,6-hexanediol, it was reported that polycarbonate diols derived from 2,2-dialkyl-1,3-propanediol are most suitable for producing APUD [44]. Acrylic polyols (polyols with acrylic polymer backbone) have been also often used since they ensure good resistance of films to water. The presence of fluorinated polyol or polysiloxane diol segments in the prepolymer-ionomer chain guarantees high film hydrophobicity and anti-adhesion properties. Interesting comparison of properties of APUD produced from mixtures of polypropylene glycol with various amounts of acrylic, polycarbonate and perfluoro-oligoether polyols was presented in [45]. Increased proportions of acrylic polyol or polycarbonate polyol resulted in decreased T_g of the polymer film (corresponding to glass transition in the soft phase of the polymer) while the presence of more perfluoro-oligoether polyol segments in the polymer chain was reflected in significantly higher *SFE*.

Still another important and quite common modification of the polymer chain in APUD synthesis is introduction of polysiloxane segments. It was proved already in the nineties that APUD forming transparent and tough films and coatings can be easily produced from poly(dimethylsiloxane) diols (PDMS diols) [46, 47]. Later, a number of papers and patents appeared dealing with such „siliconized" APUD which were synthesized also from mixtures of PDMS diols and other polyols. Detailed studies on characterization of such dispersions and films were reported, *i.a.* in [48—52]. It was found [48] that surface contact angle of films increased distinctly from *ca.* 80° starting value with increase in proportion of PDMS segments in the polymer chain up to certain level *ca.* 100—110°, depending on PDMS segment structure. It was also proved that water absorption of films made from APUD synthesized from polyol mixtures containing more PDMS was significantly lower than observed for films with lower PDMS segments content [49]. It can be anticipated that those effects were due to migration of silicone segments to the film surface that was proved by XPS investigations [53] (see also Section „Effect of polyol and isocyanate"). Even more enhanced hydrophobic properties of the film surface combined with excellent mechanical properties could be achieved when APUD were synthesized from mixtures of poly(neopentylene adipate) and polysiloxane diol having methyl and trifluoropropyl substituents on Si [54]. Comprehensive review of the literature (including patents) on APUD synthesized from PDMS diols is contained in a separate paper that will soon be published [55] which deals with all types of silicone-containing APUD with hybrid particle structure and therefore developments in that particular area of APUD will not be reviewed in detail here.

While introducing PDMS segments to prepolymer-ionomer chain results in increased hydrophobicity of films, so such APUD can be used *e.g.*, as antifouling marine coatings [56], from the other side it is desirable for certain applications to obtain more hydrophilic films. APUD which were applied for that specific purpose were synthesized based on mixtures of copolymer of propylene and ethylene oxide with poly(ethylene adipate) and it was found that good balance of water vapor permeability and water resistance needed for so called „breathable waterproof textile coatings" could be achieved for specific proportion of more and less hydrophilic polyol segments in the polymer chain [57]. Hydrophilic properties of films produced from APUD may also be increased by grafting oligomers bearing hydrophilic moieties on poly(urethane-urea) chain. Such approach was taken by the authors of two papers [58, 59] where grafting poly(ethylene glycol monomethyl ether) on poly(urethane-urea) chain was described. Another approach — also leading to increased hydrophilicity of the films produced from APUD — was to conduct synthesis of urethane prepolymer using mixture of standard polyol and sulphonated polyol sodium salt (Scheme C) [60].



Scheme C

Effect of hydrophilic group

The presence of sufficient amount of hydrophilic groups in APUD polymer chain is inevitable to avoid using additional surfactant in the process of its final emulsifying in water. From the other hand, too high proportion of such groups may result in significant decrease in resistance of films to water, so optimization of that parameter is needed. As it has already been emphasized earlier in this review commercially available APUD are dispersions of poly(urethane-urea) ionomers, *i.e.*, ionic moieties are responsible for their self-emulsifying ability, but in the very first publications and patents also APUD with nonionic moieties were reported — see *e.g.*, [61]. The reason why further research on such „nonionic" APUD was generally abandoned is their low resistance to elevated temperature which is reflected in lower storage stability. „Ionic" APUD (or „ionomer" APUD) are thermally much more stable and due to the presence of ionic groups can be easily crosslinked (see Part II of this review) what is their great advantage over „non-ionic" APUD. However, ionomer APUD suffer from poor resistance to changes in pH and to any electrolyte addition (specifically containing multivalent cations or anions) which becomes quite relevant, *e.g.*, when APUD need to be modified with fillers.

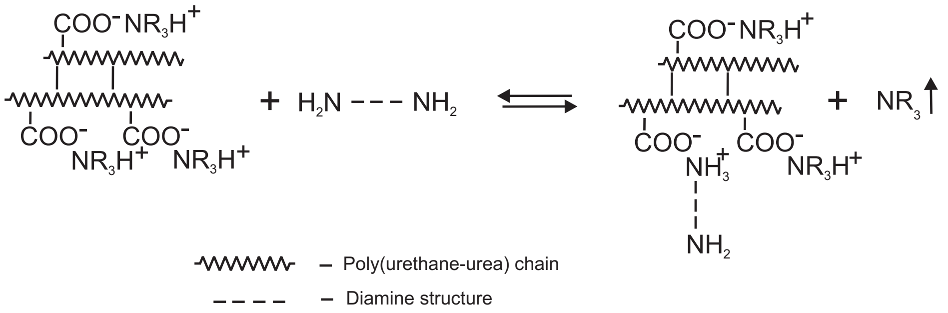
The effect of proportion of pendant COO^- groups originated from DMPA on properties of APUD and the corresponding films produced from poly(butylene adipate) and TMXDI as main starting materials was studied in [62] and it was proved that electrolytic stability of the synthesized dispersions (volume of NaCl which caused coagulation) increased when that proportion increased. In the same paper it was shown that resistance of the film to thermal degradation was diminished with increase in ionic groups amount and it was explained by lowering the hard segments content. Earlier studies *e.g.*, [63] confirmed that proportion of ionic groups affected also dispersion particle size and mechanical properties as well as T_g of films (of the soft phase of the polymer). The results of a detailed study on the effect of various factors, including concentration of ionic groups originated from DMPA, on properties of APUD synthesized from poly(ethylene adipate) and IPDI were published in [25]. It was proved that not only particle size, but also viscosity of dispersion changed significantly with changing of ionic groups content in the polymer.

As it was shown in another article published even earlier [64], polymeric gels produced by drying of anionomer APUD synthesized using higher amounts of DMPA would exhibit higher specific conductivities. In that work poly(ethylene glycol) and IPDI were used as main starting materials and LiOH was applied instead of tertiary amine as neutralizing agent. When COO^-Li^+ concentration was high enough, conductivity values of 10^{-4} mS/cm at room temperatures could be obtained what would make such gels potential materials to be used as electrolytes in lithium batteries.

Though in synthesis of anionomer APUD ionic groups are usually introduced to the polymer by using DMPA as one of the starting materials, other acids have also been applied, *e.g.*, 2-acrylamido-2-methyl-propanesulfonic acid [65]. The authors of that paper claimed that the coatings produced from such APUD exhibited better mechanical and thermal properties than coatings made from APUD synthesized using DMPA as precursor of ionic groups.

Effect of neutralizing and chain extending agent

If one considers that usually in synthesis of anionomer APUD both the neutralizing agent and the chain-extending agent are amines, so both can react with COOH



Scheme D

groups, and that chain extending reaction may be disrupted by side reaction of polyamine with COOH, it becomes clear that optimizing molar proportion of those two agents in a process of producing such APUD is of great importance. In the scheme contained in [63] the process of extension of NCO-terminated prepolymer-ionomer chain with polyamine is quite clearly visualized and the possibility of occurrence of side reaction of NCO groups with water is rightly emphasized. However, according to author of this review quite important equilibrium side reaction of ion exchange between tertiary amine and polyamine (Scheme D) has not been taken into account so far by the researchers.

It can also be assumed that if either molar excess of polyamine (with regard to NCO groups content in prepolymer-ionomer) is used in APUD synthesis or there will be not enough tertiary amine to neutralize all pendant COOH groups of urethane prepolymer to form prepolymer-ionomer, polyamine (which is originally designated as chain-extending agent) can act as neutralizing agent and — taking into account that it is multifunctional — may produce ionic crosslinks between polymer chains. Therefore, the results of any study aiming at investigation of the combined effect of neutralizing amine and chain extending amine on the properties of APUD and corresponding films should be carefully looked upon, but based on available literature data it seems that no such direct study has yet been undertaken. When the authors of paper [63] investigated the effect of changing proportions of triethylamine applied as neutralizing agent they found that the smallest particle size and the best mechanical properties were achieved when neutralization degree was 100 %, but that result was obtained for constant amount of hexamethylenediamine applied as chain extending agent corresponding to (theoretically 1/1 NCO/NH molar ratio). It could be interesting to learn what would happen to dispersion and film properties if other NCO/NH molar ratios were used. The same authors studied earlier the chain extension process in detail and found that also dispersion particle size was of great importance in terms of optimizing the amount of polyamine — the higher was particle size the higher was optimum amount of chain extender reflected in the highest value of molecular weight of the final polymer [66]. It could be explained by the fact that the process of chain extension was driven by diffusion of polyamine into the prepolymer-ionomer micelles. Nevertheless, those results clearly indicate that still more research is needed in order to understand fully the mechanism of dispersion particle formation in the process of synthesis of anionomer APUD. Interesting experiment was made by the authors of another paper [26] who first only partly neutralized the COOH groups with triethylamine (they called that process „pre-neutralization") and only after the prepolymer-ionomer had been dispersed in water the remaining portion of neutralizing amine was added (that step was called „post-neutralization"). It was quite unexpected that after the post-neutralization step both dispersion particle size and dispersion viscosity increased significantly. This phenomenon was explained by pulling out water to the insides of the particle by some portion of ionic pairs formed in post-neutralization process.

Results of a detailed study on the effect of neutralizing base on the properties of APUD obtained via „acetone" process (but methyl-ethyl ketone was used instead of acetone) showed that MeOH-neutralized APUD had smaller particle size and the corresponding films showed higher water absorption than amine-neutralized APUD [35]. Another finding from that study was that particle size and stability of APUD were higher when the neutralizing tertiary amines had longer alkyl chains due to poor hydration of the corresponding cations.

The effect of various polyamines applied as latent chain extenders in APUD containing both anionic groups and methyl-ethyl ketoxime — blocked and caprolactam — blocked NCO groups on properties of dispersions and films was investigated in a study described in [67]. It was found that in such systems de-blocking of NCO groups followed by chain extension with polyamine occurred at 60—180 °C depending on type of blocking agent and polyamine used. Such ketoxime-blocked prepolymer-ionomer can be also converted to self-crosslinkable APUD — details related to crosslinking of APUD and APUAD will be dealt with in Part II of this review.

As it has been mentioned in Section "Methods of synthesis", apart from polyamines also diols can be applied as chain extenders in synthesis of anionomer APUD [26, 68]. In that case the problem of ion exchange reactions between amines does not exist, but due to lower reactivity of diols with -NCO it is necessary to complete the chain extension before emulsifying the polymer in water to avoid competitive reaction of water with NCO. Thermal resistance of films produced from APUD synthesized using hydrazine and ethylenediamine as chain extenders was found [68] to be better than when ethylene glycol was applied as chain extender and it was explained by higher degree of hydrogen bonding in poly(urethane-urea)s formed in reaction of diamines with NCO than in polyurethanes formed in reaction of ethylene glycol with NCO.

Some specific systems were also reported [69, 70] where epoxy resin was admixed with prepolymer-ionomer which had NCO groups blocked before emulsifying it in water, so polyamine added in the next step played the role of both chain extender reacting with blocked NCO and crosslinking agent reacting with epoxy groups. In another study [71] amine-terminated epoxy-acrylic graft copolymers were applied as chain extenders/crosslinking agents in synthesis of APUD which formed coatings with enhanced properties.

Effect of co-solvent

As it has already been emphasized earlier in this paper most of the commercially available anionomer APUD contain *ca*. 5—10 % of co-solvent. Usually, NMP is the co-solvent of choice used to dilute the highly viscous prepolymer-ionomer before it is dispersed in water. While NMP facilitates coalescence of dispersion particles in the film formation process what is advantageous when APUD are applied as coatings, it remains in the film acting as plasticizer and reducing its water resistance. Based on European Regulation No. (EC) 1272/2008 NMP belongs to reproductive toxicant category 1B and APUD containing NMP have to be labeled accordingly. Therefore, certain modifications of the process of APUD synthesis which enable to obtain co-solvent free dispersions were developed. The most popular approach applied already in the early studies on APUD synthesis is to replace NMP with low-boiling solvent (*e.g.*, acetone or methyl-ethyl ketone) and distill it off in the end of the process — see the „acetone process" mentioned in the earlier text. The effect of acetone on the properties of films cast from APUD was investigated *e.g.*, in [30] and [72] and it was found [30] that if acetone was added during the reaction it remained in the film (though it was dried) and acted as internal plasticizer for the polymer that formed the film. However, if acetone was added to the already formed aqueous dispersion no such effect was observed. The process of drying of films produced from APUD was studied in detail in a PhD dissertation [73] and, *i.a.*, it was confirmed that the location of additional solvent in the film either in hard or in soft phase of the polymer depended on the polarity of the solvent. Other approaches which may allow for avoiding the use of co-solvent in APUD synthesis include „ketamine", „ketazine" and „polymer melt" processes (see Section „Methods of synthesis" for details).

In further search for a method of producing APUD without NMP, acetone or any other organic solvent a method was developed [74] and later commercialized [75] which involved preparation of high solids content dispersion of urethane prepolymer in water using static mixer and conducting chain extension with polyamine also in a high shear conditions. It was claimed that when applying this method even aromatic diisocyanates could be used as starting materials and stable solvent free APUD having solids content above 50 % could be obtained what could not be achieved if APUD were produced using other methods.

Another very effective approach to avoid NMP in APUD synthesis that led to commercialization of synthesis of NMP — free anionomer APUD is using low-reactive diisocyanates as starting materials. When TMXDI is used instead of IPDI in reaction with polyol and DMPA the viscosity of prepolymer-ionomer that is obtained after neutralization with polyamine can be reduced not by diluting it with co-solvent, but by heating it to temperature of around 90—120 °C before emulsifying in water at a temperature below 40 °C [13, 76]. Due to low reactivity of free NCO groups originating from TMXDI the prepolymer-ionomer does not react with water before polyamine is added to complete the process. Presently, quite a few grades of NMP — free APUD produced using TMXDI are available on the market.

Still another approach to anionomer APUD synthesis which also resulted in obtaining solvent — free dispersions was synthesis of APUAD through diluting the prepolymer-ionomer with a radically polymerizing monomer, *e.g.*, acrylic ester, followed by emulsifying in water, chain extension with polyamine and emulsion polymerization of that monomer. APUAD thus obtained combined the properties of both polyurethanes and acrylic polymers and different relevant technologies were developed and later commercialized. Synthesis and characterization of APUAD will be discussed in Part II of this review.

CONCLUSIONS

Aqueous polyurethane dispersions (APUD) are among most developing sectors of polyurethane materials with annual market increase of *ca*. 5 % per annum. The review of developments in APUD technology revealed that since first commercialization of those products certain important improvements have been made with regard to APUD synthesis including, *i.a.*,:

— development of processes of APUD synthesis without co-solvent,

— combining the advantages of polyurethanes and acrylic polymers and lowering the production cost through development of aqueous polyurethane-acrylic dispersions (APUAD) with hybrid particle structure,

— combining the advantages of polyurethanes and silicones through development of APUD synthesized from poly(dimethylsiloxane) diols,

— synthesizing APUD from renewable materials, specifically from castor or soybean oil.

Despite the above developments there is still room for new research which may be focused on investigation of: (1) the combined effect of neutralizing amine and chain extending amine on the properties of APUD and corresponding films and coatings, (2) the mechanism of dispersion particle formation and the effect of various factors on dispersion particle morphology, especially in the case of APUD produced from polyols containing strongly hydrophobic segments, *e.g.*, poly(dimethylsiloxane) or fluorinated alkyl chains, and (3) the possibility of applying the known processes of APUD synthesis for development of functional hybrid materials with entirely new properties.

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