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

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Abstract: Part I of the review that concerns the developments in aqueous polyurethane dispersions (APUD) and aqueous polyurethane-acrylic dispersions (APUAD) technology was recently published. In the present paper (constituting Part II of the review) synthesis and characterization of aqueous polyurethane-acrylic dispersions (APUAD) which have hybrid particle structure and produce films and coatings exhibiting much better properties than those produced from blends of APUD and acrylic polymer dispersions are reviewed based on recent literature data. Possibilities of crosslinking the films and coatings produced from APUD and APUAD and of obtaining filled composites, specifically nanocomposites, from those dispersions are also demonstrated, and currently reported applications of those dispersions are briefly summarized. The most important developments and areas where further research may still be required are suggested with regard to synthesis and characterization of APUAD as well as to crosslinked and filled systems involving APUD or APUAD.

Keywords: polyurethane dispersions, polyurethane-acrylic dispersions, ionomers, coatings, adhesives, crosslinking, nanofillers, nanocomposites.

Postępy w technologii wodnych dyspersji poliuretanowych i poliuretanowo-akrylowych. Cz. II. Dyspersje poliuretanowo-akrylowe oraz modyfikacja dyspersji poliuretanowych i poliuretanowo-akrylowych

Streszczenie: Artykuł stanowi część II przeglądu literaturowego dotyczącego postępów w technologii wodnych dyspersji poliuretanowych (APUD) i poliuretanowo-akrylowych (APUAD). Omówiono syntezę i właściwości APUAD o hybrydowej budowie cząstek, z których otrzymuje się filmy i powłoki o właściwościach znacznie lepszych niż właściwości powłok uzyskiwanych z mieszanin APUD i dyspersji polimerów akrylowych. Przedstawiono możliwości sieciowania filmów i powłok wytwarzanych z APUD i APUAD oraz otrzymywania z nich napełnionych kompozytów i nanokompozytów, podano

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też informacje na temat ich obecnych zastosowań. Zaprezentowano najważniejsze osiągnięcia dotyczące syntezy i badań właściwości APUAD oraz usieciowanych i napełnionych systemów zawierających APUD lub APUAD, wskazano obszary, w których dalsze badania wciąż jeszcze mogą być potrzebne.

Słowa kluczowe: dyspersje poliuretanowe, dyspersje poliuretanowo-akrylowe, jonomery, materiały powłokowe, kleje, sieciowanie, nanonapełniacze, nanokompozyty.

AQUEOUS POLYURETHANE-ACRYLIC DISPERSIONS

Developments in technology of aqueous polyurethane1) dispersions (APUD), especially with regard to anionomer APUD, were discussed in a review paper published recently [1]. It was emphasized there that a very important modification of the properties of APUD was producing hybrid aqueous polyurethane-acrylic dispersions (APUAD). Possibility of combining APUD and acrylic aqueous dispersions (AAD) has been widely investigated in the recent decades since it was anticipated that hybrids obtained in that way would exhibit advantageous features of both polyurethane and acrylic polymer. Despite the existence of early patents which dealt with hybrid polyurethane-acrylic dispersions synthesized by emulsion polymerization of acrylic monomers in APUD, *e.g.* [2], and short notes in some papers, *e.g.* [3], until the nineties in practice only blends of APUD and AAD were commercially available and their properties were claimed to combine properties of both polymers, specifically when they were co-crosslinked [4]. Even at present the reports dealing with simple blends of APUD and AAD can be still found in the literature [5]. Probably the first communication where the properties of true hybrid polyurethane-acrylic dispersions (APUAD) were described was presented at a major international conference [6] and two years later the relevant paper was published [7]. Some papers dealing with the same subject were published still in the nineties [8—10]. In the years which followed a number of studies dealing with synthesis and characterization of APUAD were conducted [11—29] and in 2009 a relevant review was published [30]. In those studies the most common acrylic esters as well as other common monomers like *e.g.* styrene were applied, but in some papers the use of certain specific acrylic monomers in synthesis of APUAD which imparted specific features to films or coatings was proposed. Examples are the use of glycidyl methacrylate reported in [27] or fluorinated acrylic esters reported in [31] and [32].

The most common method of APUAD synthesis is emulsion polymerization of acrylic monomers in APUD. Both seeded emulsion polymerization where acrylic monomers were added stepwise to the seed APUD and batch emulsion polymerization where the acrylic monomers were admixed with APUD and later polymerized were reported. APUAD can also be produced by using acrylic monomers as active diluents in the process of APUD synthesis and conducting emulsion polymerization only after emulsifying the solution of polyurethane polymer in water. Miniemulsion polymerization seems also to be applied widely and effectively by the researchers to produce APUAD. It is anticipated that in all those methods grafting of the monomers on the polyurethane or polyurethane-urea chain may proceed along with the

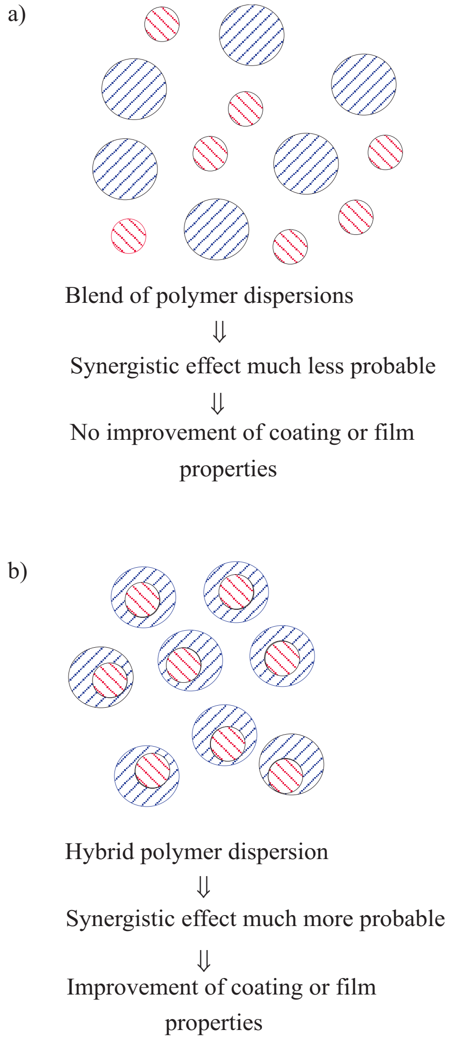

Fig. 1. Differences between: a) the particles with homogeneous structure contained in a blend of aqueous dispersions of two polymers, b) the particles with hybrid structure contained in a dispersion obtained by polymerization of a monomer of one polymer in an aqueous dispersion of another polymer which result in different properties of corresponding films and coatings produced from such dispersions

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1) 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).

emulsion polymerization, so the resulting dispersions are supposed to have hybrid, *e.g.* core-shell, morphology due to limited compatibility of both polymers. Schematic picture of possible structure of a core-shell dispersion particle that is supposed to be formed in emulsion polymerization of acrylic monomers in anionomer APUD can be found in [33].

When the properties of simple APUD-AAD blends and of hybrid APUAD produced by polymerization of acrylic monomers either during APUD synthesis or in a ready-made APUD, were compared it appeared obvious that using APUAD much better properties of films and coatings could be achieved [34—39]. The reason for that was hybrid structure of dispersion particles in case of APUAD which allowed for direct interactions between polyurethane backbone and acrylic polymer chains partly grafted onto that backbone and created possibility for synergistic effects to occur (Fig. 1.)

The hybrid structure of APUAD particles was proved, *inter alia*, in [39] where comparison of TEM images of particles of APUAD and blend of APUD with AAD with exactly the same overall composition was made. The authors of that paper claimed that the core-shell structure of APUAD particles was obtained.

In the other publications, *e.g.* [35—38] it was proved that mechanical properties of coatings and films produced from APUAD were much better than observed for those produced from corresponding APUD/AAD blends, specifically when proportion of polyurethane component to acrylic component was lower than 50 %. However, it is to be noted that synergistic effect observed in APUAD depends on the method of their preparation. Various approaches to APUAD synthesis were investigated and for each approach a mechanism of hybrid dispersion particle formation was proposed in a study described in [13]. Three methods were applied in that study: (1) seeded emulsion polymerization of a mixture of acrylic and styrene monomers in APUD, (2) diluting the prepolymer-ionomer with the same monomers, emulsifying it in water and conducting chain extension of prepolymer-ionomer chain with polyamine followed by emulsion polymerization and (3) synthesis of polyurethane anionomer in AAD conducted by diluting the prepolymer-ionomer with the same monomers and emulsifying prepolymer-ionomer in AAD followed by chain extension with polyamine. *Inter alia*, it was found that method (2) led to a specific morphology of APUAD particles which the authors called „embedded sphere" since a „sphere" of acrylic polymer was embedded in APUD particle (Fig. 2.)

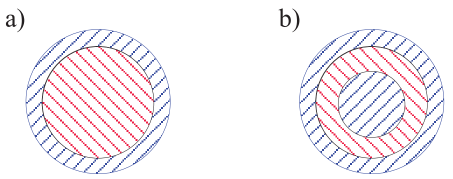


Fig. 2. Comparison of: a) "core-shell", b) "embedded sphere" of APUAD particle morphologies

Formation of that structure can be explained by the fact that the APUD particles were actually swelled by the monomers before emulsion polymerization started, so polymerization proceeded mostly inside the particles, and after acrylic-styrene copolymer was formed phase separation occurred leading to „embedded sphere" morphology.

Comparison of dispersion particle morphologies observed in synthesis of APUAD with various compositions of polyurethane and acrylic polymer parts by emulsion polymerization and miniemulsion polymerization was investigated by the authors of [37] who also reported that different synthetic routes led to different particle structures. Though APUAD particle morphologies and film structures were studied in certain other works, *e.g.* [15, 25, 36, 39] it seems that further investigations are still needed which would clarify the relationship between APUAD particle morphology and film structure and the preparation method as well as the proportion and chemical structure of polyurethane and acrylic polymer components. Though most probably the majority of APUAD available on the market are produced using emulsion polymerization, preparation of APUAD using both emulsion polymerization [33, 39—42] and miniemulsion technique [43—48] was described in more recent papers published on APUAD. In some of those studies the polyurethane backbone was terminated with hydroxyl-functional acrylate monomer, so polyurethane „macromer" [49] was obtained which could co-polymerize with acrylic monomers. Reactions proceeding in the process of synthesis of APUAD using miniemulsion technique involving polyurethane „macromer" formation step described in [43] is presented in Scheme A and schematic visualization of possible structures occurring in dispersion particles obtained in such process is presented in Fig. 3. It should be noted that in a process described in that paper anionic surfactant was applied, so the presence of hydrophilic groups in polyurethane chain was not required to obtain aqueous dispersion.

AFM investigations of individual particles of APUAD synthesized using miniemulsion technique were conducted in a study reported in another paper [44] and for certain composition of acrylic monomers it was found that viscoelastic properties of the particles were broadly uniform — see Fig. 4 where AFM images of the particles are shown. The phase contrast at the particle peripheries was attributed to the greater AFM tip interactions with mica substrate.

Recently, an interesting method of synthesis of APUAD via miniemulsion polymerization was reported in [47] and [48]. The authors of those papers conducted continuous polymerization of miniemulsions containing APUD and mixture of acrylic monomers initiated by UV light and carried out in the especially designed tubular reactor. The resulting dispersions were successfully tested as pressure-sensitive adhesives.

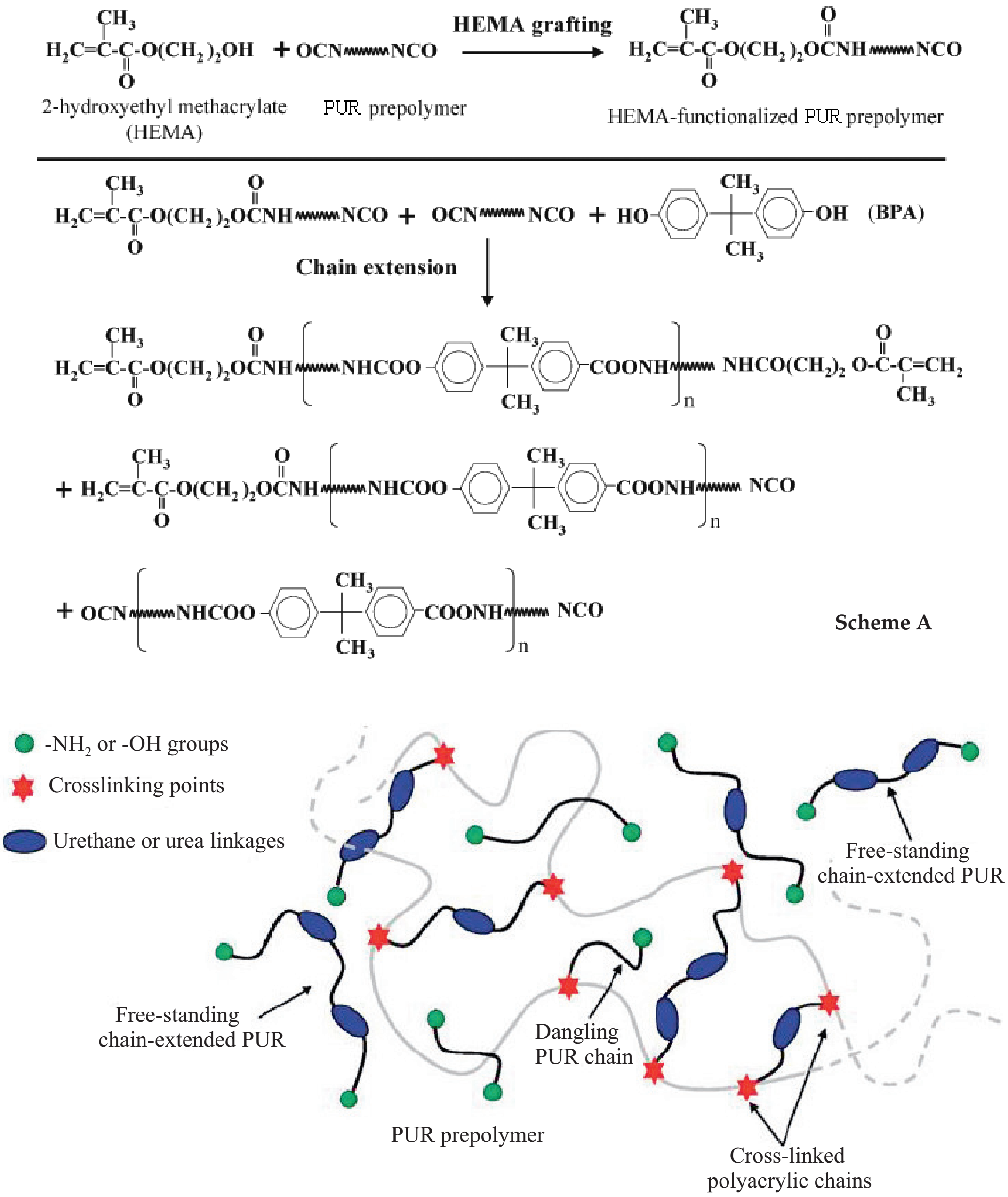


Fig. 3. Schematic visualization of possible structures occurring in particles of APUAD produced in miniemulsion process [43]

CROSSLINKING OF FILMS AND COATINGS PRODUCED FROM AQUEOUS POLYURETHANE AND POLYURETHANE-ACRYLIC DISPERSIONS

Crosslinking through double bonds

If unsaturated moieties are introduced in the structure of a polyurethane or poly(urethane-urea) polymer it can be crosslinked either by UV or through oxidative drying (self-crosslinking) [50] which leads to improved mechanical strength and chemical resistance of films or coatings produced from such APUD or APUAD dispersions. Several papers were dealing with synthesis of such dispersions where acrylic monomers with hydroxyl functionality were used to terminate polymer backbone [51, 52] or unsaturated diols (usually alkyd-type unsaturated polyesters) [53—59] were applied as polyol components. The authors of [52] synthesized APUD containing anionomers terminated with unsaturated bonds and exhibiting different functionalities in UV-curing by applying ethylenediamine and diethylenetriamine as prepolymer-ionomer chain extending agents, and investigated the effect of the polymer functionality on properties of APUD and corresponding UV-cured films.

The effect of structure of alkyd-type polyol on properties of dispersions and related coatings was studied in detail in [54] and it was found, *inter alia*, that the superior dispersion stability and coating hardness was achieved for APUD produced from polyester synthesized from isophtalic acid and maleic anhydride. A detailed study on synthesis of APUD and APUAD from polyol mixture containing unsaturated diol and on characterization of

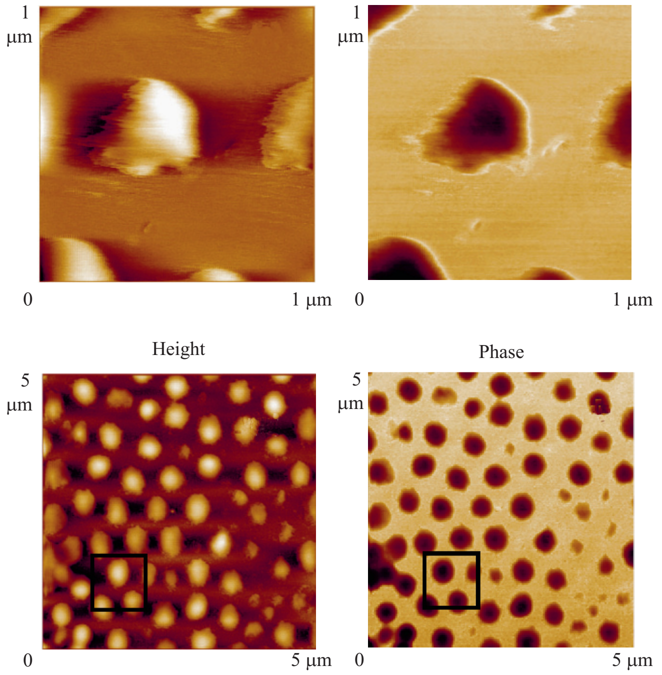


Fig. 4. AFM images of individual particles of APUAD synthesized using miniemulsion technique taken on a mica substrate; a), b) are higher resolution images taken from the zones marked with squares on c) and d), respectively [44]

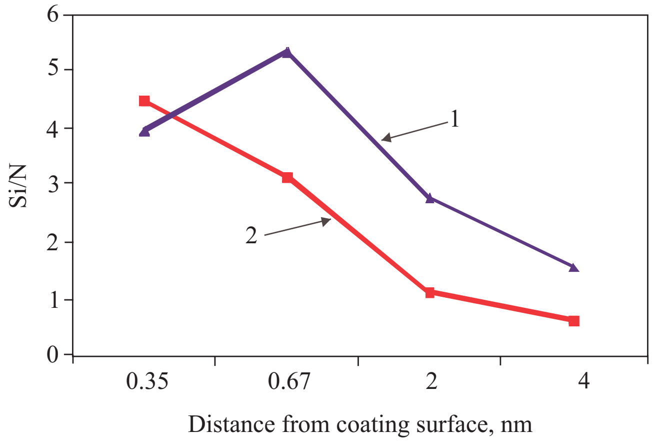


Fig. 5. Dependence of Si content (expressed as Si/N ratio) in UV-cured coatings produced from poly(siloxaneurethane-urea) / acrylic-styrene APUAD (1) and from starting poly(siloxane-urethaneurea) APUD (2) on distance from coating surface as shown by XPS — based on data obtained in a study described in [53]

corresponding films and coatings was presented in [53]. The authors of that paper investigated APUD synthesized using mixtures of polytetramethylene glycol, PDMS diol and unsaturated diol and APUAD obtained by emulsion polymerization of a mixture of acrylic monomers and styrene in such APUD. A designed factorial experiment was made in order to predict the effect of three variables on the properties of dispersions and films: (1) content of acrylic-styrene polymer part in dispersion solids, (2) content of unsaturated diol in the polyol mixture and (3) content of PDMS diol in the polyol mixture. Both UV curing and air drying led to distinct increase in coating hardness and was reflected in mechanical properties of films what proved that crosslinking actually occurred. Based on the observed complex relationship between coating hardness and unsaturated segment content in the polymer backbone it was anticipated that in APUAD synthesis grafting of acrylic and styrene monomers on the polymer chain actually took place. It was also proved by XPS (ESCA) investigations that in the case of APUD and APUAD which were synthesized using PDMS diols silicone segments migrated to the surface making it strongly hydrophobic and the concentration of Si distinctly increased with diminishing distance from the surface (Fig. 5). It is worth to note that migration of silicone segments to the surface was much more distinct in case of APUAD than for starting APUD what could be explained by much stronger phase separation in coatings produced from APUAD.

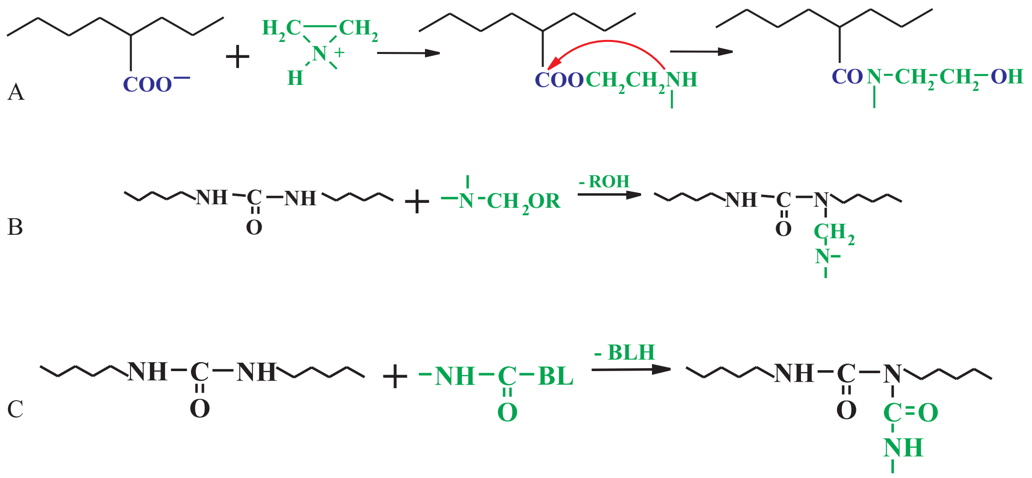
Synthesis of UV-curable APUAD containing PDMS segments in the polymer chain from blend of acrylic-functionalized polyol (derived from soybean oil), polysiloxane diol and butanediol was recently reported in [59]. In the process described in that paper the prepolymer-ionomer chain was terminated with OH-functional acrylic monomers, alcohols or fluorinated alcohols. It was found that increased crosslinking density resulted in increased contact angle of films produced from such APUAD.

Other methods of crosslinking

Self-crosslinking via azometine formation or hydrolysis of alkoxysilane groups

A method of synthesis of self-crosslinked APUD and APUAD, alternative to introducing double bonds capable of oxidative crosslinking (see further text for details), was revealed in [60] and [61]. That idea was based on ability of ketones to react with amines forming azometine group $(R_1R_2)C=N-R_3$, but only in acidic media. Thus, if a carbonyl-functional diol was used as starting material for urethane prepolymer synthesis, final polymer also contained carbonyl groups. If diamine was added to such APUD no reaction proceeded between amino and carbonyl groups since anionomer APUD was slightly basic. Then, after the film was formed triethylamine applied as neutralizing agent evaporated and COOH groups were released what allowed diamine to react with carbonyl groups of the polymer forming crosslinks. Although coatings with good hardness were obtained from such APUD (and APUAD), a significant drawback of that system was low resistance to water, specifically at higher crosslinking densities which could be explained by hydrolysis of azometine bonds.

Another possibility of obtaining a self-crosslinkable APUD was described in [60]. Prepolymer-ionomer was obtained in a standard way and the terminal NCO groups



Scheme B

were blocked with methyl ethyl ketoxime. Then, the resulting product was emulsified in water. Next step was reaction of blocked prepolymer-ionomer with *N*-phenylaminopropyltrimethoxysilane leading to de-blocking of NCO groups and formation of trimethoxysilane terminal groups. Since trimethoxysilane groups do not tend to hydrolyze in basic conditions, the resulting APUD was stable during storage, but — similarly as in the case of azometine system described earlier — hydrolysis and subsequent crosslinking proceeded when triethylamine was released from the film during drying and pH changed to acidic.

Two-component systems

Possibility of crosslinking the films and coatings produced from APUD in order to enhance their mechanical properties and chemical resistance was reported already in the eighties [3, 63] and later 2 reviews dealing with two-component waterborne polyurethane systems including APUD were published [64, 65]. Several commercially available crosslinking agents including polyaziridine, polycarbodiimide, epoxysilane, water-dispersed polyizocyanate and melamine-formaldehyde were compared as crosslinkers for APUD [66]. Polyaziridine, polycarbodiimide, epoxysilane and water-dispersible polyisocyanate reacted at room temperature while melamine-formaldehyde resin required 120 °C for effective crosslinking. It was found that polyaziridine crosslinking allowed to achieve the best mechanical properties and solvent resistance of coatings. Polyaziridines, and melamine-formaldehyde resins were evaluated as crosslinkers for APUD *e.g.* in [67, 68], respectively, and two-component systems designed for automotive clear-coats based on APUD and on acrylic polyols, cured with water-dispersible polyisocyanates and containing different catalysts specific for NCO–OH reaction, were compared in [69]. Presently, three types of crosslinkers are used in most of two-component APUD systems offered on the market: polyaziridines (for room temperature curing) and melamine-formaldehyde resins or water-dispersible blocked polyisocyanates (for elevated temperature curing). Simplified schemes of reactions taking place when those crosslinking agents are applied in APUD or APUAD are shown in Scheme B.

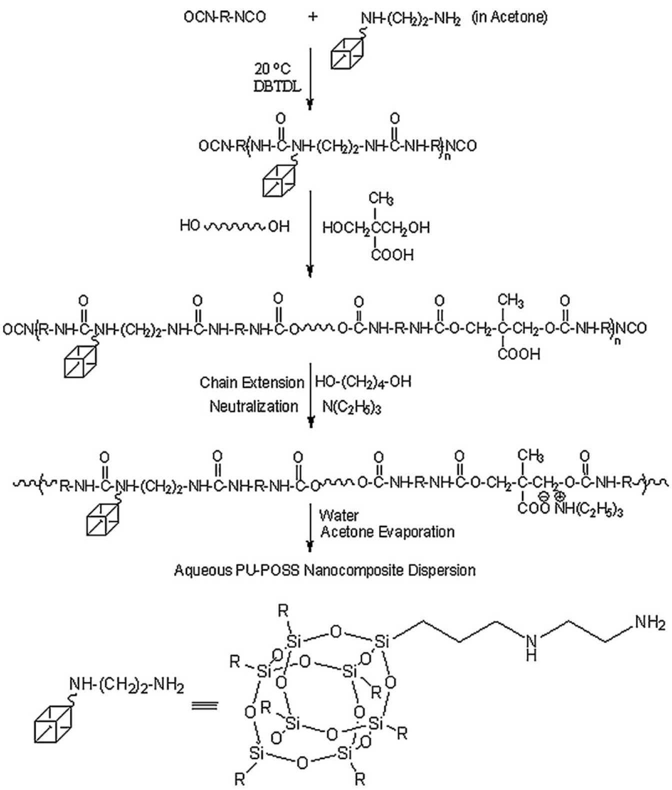
AQUEOUS POLYURETHANE AND POLYURETHANE-ACRYLIC DISPERSIONS CONTAINING FILLERS

APUD have relatively much lower viscosities as compared to standard aqueous dispersions of acrylic, styrene or vinyl polymers and copolymers, so sedimentation may occur if they are modified with mineral fillers. Therefore, addition of pigment dispersants and thickeners as well as applying special techniques like *e.g.* using ultrasonic treatment [70—72] were recommended to achieve good suspension of fillers in APUD and it was found [70, 72] that this method was the most effective in terms of achieving good film properties when fillers were added to water in which prepolymer-ionomer was emulsified. Addition of fillers to polyol before synthesis of APUD is also a good way to reach good stability of filled dispersion. In the last decade a few papers dealing with APUD and APUAD modified with nanofillers that way were published, *e.g.* [73—75]. In a study published in [74] waterborne polyurethane/organophilic clay nanocomposites were obtained in a „prepolymer-ionomer" process from polyol/exfoliated nanoclay hybrid obtained by heating of commercial hydrophilic modified nanoclay with polyol at elevated temperature for few hours. Exfoliation of nanoclay by polyol was confirmed by X-ray diffraction. Films obtained from the modified APUD showed enhanced mechanical properties as well as thermal and water resistance. APUD containing the same type of hydrophilic modified commercially available nanoclay, was obtained in the same manner [75], but before of neutralization of prepolymer-ionomer part of NCO groups was reacted with 3-(phenylaminopropyl)trimethoxysilane, so eventually silylated crosslinkable APUD was obtained. Finally [76], APUAD containing the same type of nanoclay, but intercalated by the authors of that paper using 3-aminopropyltrimethoxysilane, was synthesized via emulsion polymerization of mixture of methyl methacrylate and methacryloxypropyltrimethoxysilane in a silylated APUD obtained as reported in [75], *i.e.* modified with hydrophilic silane-intercalated nanoclay.

Waterborne anionomer APUD-based nanocomposites involving dihydroxy- and diamino-functional POSS (polyhedral oligomeric silsesquioxanes) were synthesized by the authors of studies reported in [73] and [76]. First, POSS samples were dissolved in acetone and reacted with diisocyanate. In the next steps the resulting POSS moieties-containing NCO-terminated oligomer was reacted with polyol and DMPA and the process was completed by chain extension with butanediol, neutralization of COOH groups of prepolymer-ionomer, emulsifying the polymer in water and distillation of acetone (see Scheme C) [73]. It was proved by X-ray investigations that "POSS cages maintained self-assembling ability with formation of nanocrystal phase". However, the overall structure of the film appeared to be more smooth for POSS containing samples. Dramatic increase in tensile strength and moderate decrease in elongation at break was observed with increasing POSS content in the film.

A different approach to synthesis of POSS-modified APUAD was very recently proposed [78]. In that study, methacryloilo-functional POSS was used as a reactive modifier of UV-curable APUAD. Also recently, SiO_2-modified APUAD were synthesized from APUAD containing trimethoxysilane groups by modification with hydrolyzed tetraethoxysilane (TEOS). It was reported that the film structure depended on the proportion of TEOS to APUAD and that mechanical properties of the films were distinctly improved as compared to unmodified APUAD [79].

APUAD modified with graphene oxide were also recently studied [80, 81] and it was found that just 0.015 % of that nanofiller was sufficient to obtain much improved water resistance of the film while higher amounts were not as effective in that regard. Other nanofillers — nano ZnO and superparamagnetic iron oxide (SPIO) were also used for modification of APUD [71, 82] and nanosilver was used for modification of 2-component waterborne polyurethane based on water-dispersible polyol — water-dispersible polyisocyanate system [83]. In a study reported in [71] coatings produced from APUD containing two different amounts of nano ZnO (0.1 % and 1 %) were tested and (similarly as it was shown for graphene oxide modified APUAD) it was found that a very small amount of nanofiller (it was 0.1 % in case of nano ZnO) was sufficient to get all substantial coating properties (abrasion resistance, hardness and water resistance) significantly improved as compared to unmodified APUD while the properties of coatings containing 1 % of that filler were not as good. In another study published very recently [82] SPIO



Scheme C

a) b) c)

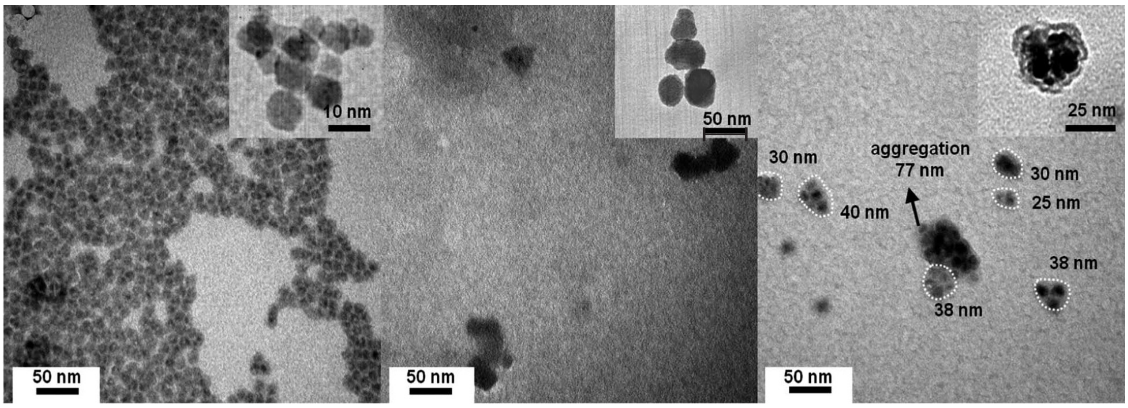


Fig. 6. TEM image of: a) SPIO particles, b) APUD particles, c) SPIO-containing APUD particles [82]

was admixed with prepolymer ionomer before emulsifying in water and chain extension has been completed, so APUD containing SPIO particles could be obtained. The formation of APUD particles containing SPIO was confirmed by TEM (Fig. 6).

The observed decreased size of APUD-SPIO hybrid particles as compared to unmodified APUD particles was explained by interaction of SPIO with hard segments of the poly(urethane-urea) ionomer.

Cellulose nanocrystals constitute another interesting class of nanofillers [84—86] which recently was investigated in certain applications, including modification of APUD [87, 88]. In the study reported in [87] suspension of cellulose nanocrystals was simply mixed with APUD. Though the mechanical strength of the films produced with modified APUD was distinctly higher than that of films produced from the unmodified APUD, the former films exhibited much lower elongation at break. In another study [88] the cellulose nanofiller was incorporated *in situ*, *i.e.* before the reaction started and it was found that part of it was actually grafted on the (polyurethane-urea) polymer. In that case modification with cellulose nanocrystals led to significant increase in thermal properties and mechanical strength of films produced from APUD without affecting much the film flexibility.

APPLICATIONS OF AQUEOUS POLYURETHANE AND POLYURETHANE-ACRYLIC DISPERSIONS

A detailed list of possible applications of APUD was presented in [89] based partly on data reported in [90]. Undoubtedly APUD and APUAD are used predominantly as coating binders and depending on their chemical structure both hard coatings designated for wood, metals, plastics or masonry, exhibiting excellent abrasion and chemical resistance combined with flexibility, and soft-feel elastic coats for leather or textiles can be produced based on those dispersions. Typical examples of coating applications include parquet flooring, furniture finishes, automobile lacquers and dashboard covers. Specific advantage of using APUD as corrosion protection coatings on metal substrates was discussed in [91] and [92]. More details on various coating applications of APUD and APUAD can be found in *e.g.* [19, 53, 55, 59, 71, 93—104]. Other important current and potential applications of APUD and APUAD include, *inter alia*:

— adhesives, especially for footwear, textile and packaging industry [43, 44, 47, 48, 57, 68, 101—111];

— leather finishes and substrates for artificial leather production [112—116];

— binders for inks [117];

— binders for ceramic powders [118—123];

— semi-permeation membranes [124, 125];

— single-ion electrolytes in batteries [126—128];

— paper sizing agents [129, 130];

— retanning agents for collagen fibres (APUD containing pendant fluorescent groups in a polymer chain) [131].

CONCLUSIONS

The possibility of combining the properties of aqueous polyurethane dispersions (APUD) and aqueous acrylic dispersions (AAD) had been widely investigated over last few decades. It was confirmed that hybrid aqueous polyurethane-acrylic dispersions (APUAD) obtained through emulsion (or miniemulsion) polymerization of acrylic monomers either in APUD or *in situ* during the process of APUD synthesis produce films and coatings which exhibit enhanced properties as compared to physical blends of APUD and AAD due to synergistic effect. Additional crosslinking of a polymer contained in APUD or APUAD allowed for improvements of mechanical properties of the films. Various crosslinkers, including polyaziridines, melamine resins or blocked polyisocyanates are commercially available. Self-crosslinking systems were also developed. Modification of APUD or APUAD with fillers, especially nanofillers like *e.g.* nanoclay, nano ZnO or cellulose nanocrystals also led to significant improvement of mechanical and thermal properties of the films produced from APUD or APUAD. Currently the main application of APUD and APUAD is in the coatings and adhesives industry, but other applications like *e.g.* leather finishes, ceramic binders, semi-permeable membranes, paper-sizing agents or membranes for lithium batteries have also been investigated.

Further research which still seems to be needed in the area of APUAD may involve investigation of the mechanism of dispersion particle formation and the effect of various factors on dispersion particle morphology as well as extension of studies on producing APUAD from APUD via UV-initiated continuous emulsion (or miniemulsion) polymerization which have already started. Undoubtedly, more research is also needed in the area of self-crosslinking systems which involve APUD or APUAD. Producing composites from APUD or APUAD using new nanofillers like *e.g.* cellulose nanocrystals or fillers like supermagnetic iron oxide or POSS which impart specific properties to the composites seems also be an attractive direction of further studies involving those dispersions.

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