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Advanced polymeric materials-based on waterborne polyurethane-acrylic hybrids

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***Abstract**:*
Polyurethane-acrylate polymersare a modern class of polyurethanes hybrid which synthesizedby the reaction of diisocyanates and polyols and capped with acrylates.Due to their high mechanical stability, toughness, adhesion, durability, biological and chemical resistance, polyurethane-acrylate hybrids have become the focus of research and development in various fields.The demand for modification of polyurethane-acrylate hybrids for improved properties is constantly increasing. Polyurethane-acrylic hybrids are used as important binders in the coating industry due to their extraordinary properties.This brief review presents a summary of water-basedemulsion waterborne polyurethane-acrylic hybrids.

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I. Introduction:

Acrylic-polyurethane hybrid! The name sounds like a wonderful combination of science and technology. It is actually a wonderful combination of polyurethane and acrylic, which has brought a revolution in the binder and coating industry. But why? Because they have the secret of high-performance hidden in them! This hybrid not only disperses pigments beautifully, but its cost is also much lower. It doesn't end here, the extraordinary properties of polyurethane, such as chemical resistance, adhesion, durability, strength and mechanical stability, make this hybrid even more attractive. Now the question is, how is this hybrid made? Behind it lies the magic of NCO (isocyanate). This hybrid is made by terminating the urethane prepolymer and utilizing the functionality of acrylic. What's more interesting is that the viscosity is reduced by adding vinyl monomer, which makes processing easier and more efficient. The properties of this hybrid depend on the type, density, ratio and molecular weight of the raw materials of polyurethane and acrylic. In a word, it is a perfect combination of science and engineering, which is taking modern industry to new horizons. So, haven't you been captivated by the magic of this hybrid yet? It is not just a materials, it is a shining star of future technology! [1-10]

Polyester or polyether polyol-based urethane oligomers, which have a relatively low glass transition temperature (Tg), are a widely discussed material in industry and research. Polyether polyols are known for their hydrolytic stability, improved low temperature performance, and resistance to fungi. On the other hand, polyester polyols are unique in providing significant abrasion resistance, toughness, ozone resistance, high tear strength, and polarity. Due to the variable structure and properties of these polyols, the role of polyols and diisocyanates is very important in the synthesis of acrylic-polyurethane hybrids. In this process, the polyol first reacts with the diisocyanate and is then covered with hydroxyl ethacrylate, which increases the diversity and quality of the product. To combine the unique properties of polyurethane and acrylic polymers, the addition method and the emulsion polymerization method are used. These processes produce closely homogeneous latexes, which are widely used in industry and research. These hybrid materials are highly valued for their high performance, durability, and versatile applications. In short, urethane oligomers based on polyester and polyether polyols are a remarkable innovation in modern materials science, which has opened the door to new possibilities in the fields of industry and technology [11-18].

Emulsion waterborne polyurethane/acrylic hybrids, which use anionic, cationic and non-ionic surfactants as well as acrylic monomers containing hydroxyl groups to form water-based hybrids. This method is environmentally friendly and helpful in producing high-performance materials.this method demonstrates the diversity and versatility of polyurethane/acrylic hybrids, which is widely used in modern industry and technology.

Emulsion waterborne polyurethane/acrylic hybrids:

Lee et al. 2013 [19] and Sukhvipat et al. 2020 [20] have analyzed the development and stability of water-based poly(urethane-urea) and hybrid materials in detail. High-performance emulsions were prepared by adding various acrylate compounds such as n-butyl acrylate (BA), glycidyl methacrylate (GMA) and perfluorodecylacrylate, which were stable within the range of 40 wt% acrylic monomers (**Figure 1C**). The study showed that high acrylate content improves the molecular structure, hardness and thermal stability of the emulsion, but it may cause a decrease in consistency and increase in water absorption. On the other hand, Sukhvipat et al. [20] developed a durable water-based polyurethane using a combination of hydroxyl telechelic and hydroxylated oils, which exhibited excellent stability with 16% solids and was able to form high-quality coatings. In addition, the addition of butyl acrylate (BA) and methyl methacrylate (MMA) has further improved the mechanical properties, moisture resistance, and bonding strength of water-based polyurethanes (**Figure 1A &B**). These studies open up new possibilities for developing eco-friendly and high-performance materials, which can play an important role in industry and research.

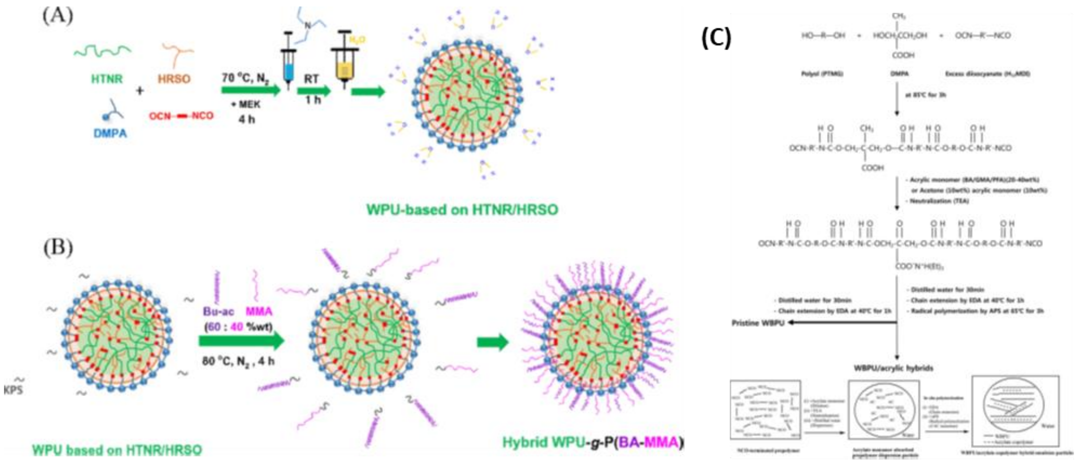

Figure 1. (A) Synthesis of WPU based on HTNR/HRSO, and (B) synthesis of hybrid WPU-g-P(MA/PMMA). (C) Preparation process of pristine WBPU and WBPU/acrylic hybrids.

A water-based hydroxyl-functionalized polyurethane/acrylic emulsion was developed in 2015 [21], which is a copolymerization of hydroxyethyl acrylate (HEA) and butyl acrylate (BA) with methyl methacrylate and acrylic-terminated polyurethane dispersions (**Figure 2A**). The study showed that increasing the HEA/BA ratio resulted in smaller molecular size, narrower size distribution, and increased emulsion stability. Films prepared by this process exhibited improved heat resistance, strong adhesion, rigidity, and hardness. However, water resistance decreased and moisture absorption increased due to the high HEA/BA ratio. The two-part coating further improved water resistance, moisture reduction, glass transition temperature, thermal stability, adhesion, rigidity, and hardness. The presence of hydroxyl groups in polyurethanes facilitates hydrogen bonding with polyisocyanates and forms a cross-linked network, which enhances the performance and durability of the coating. In 2020 [22], Liu and his colleagues modified the styrene/butyl acrylate ratio to produce semi-gloss aqueous polyurethane-polyacrylate hybrid dispersions, which exhibited excellent adhesion and toughness (**Figure 2B**).

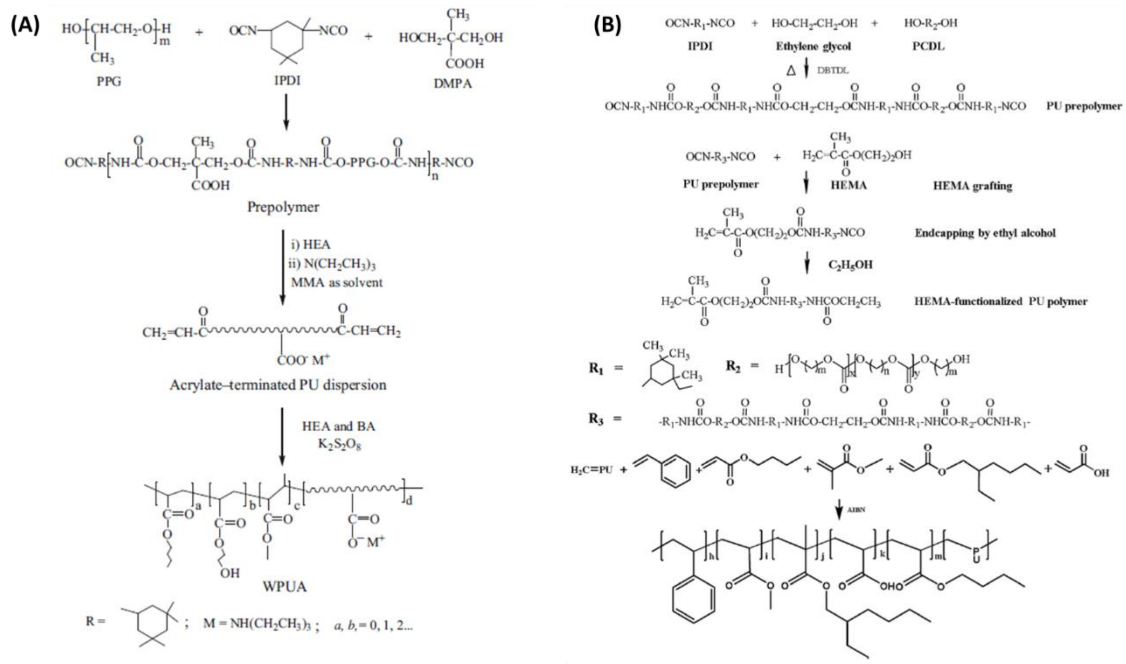

Figure 2. The preparation process of PUA hybrid emulsion.

In 2014 [23], Qiu and his colleagues prepared semi-batch acrylic-polyurethane emulsions by combining acrylic monomers and isocyanate-terminated polyurethanes. In their study, they analyzed the effect of polyurethane on the emulsion structure and film properties. With increasing polyurethane content, the film surface became stiffer and the UV transmittance decreased, which was related to the change in surface roughness. Electrophoresis application and drying at 120°C resulted in an increase in mechanical properties and a decrease in gloss of 4.0 in the film, indicating the potential for electrophoresis-based applications. In 2018 [24], Alvarez and his colleagues examined the properties of aqueous polyurethane/acrylate dispersions with bisphenol-a-glycidyldimethacrylate. The aqueous polyurethane/acrylate dispersions were prepared using a prepolymer self-emulsification method (**Figure 3**). Increasing the bisphenol-a-glycidyldimethacrylate/1,4-butanediol ratio increased the polymer chain length, resulting in lower viscosity and stable dispersions, although the solids content was higher. Adding 35 wt% bisphenol-a-glycidyldimethacrylate improved the adhesion strength of the coating by increasing the cross-linking density.

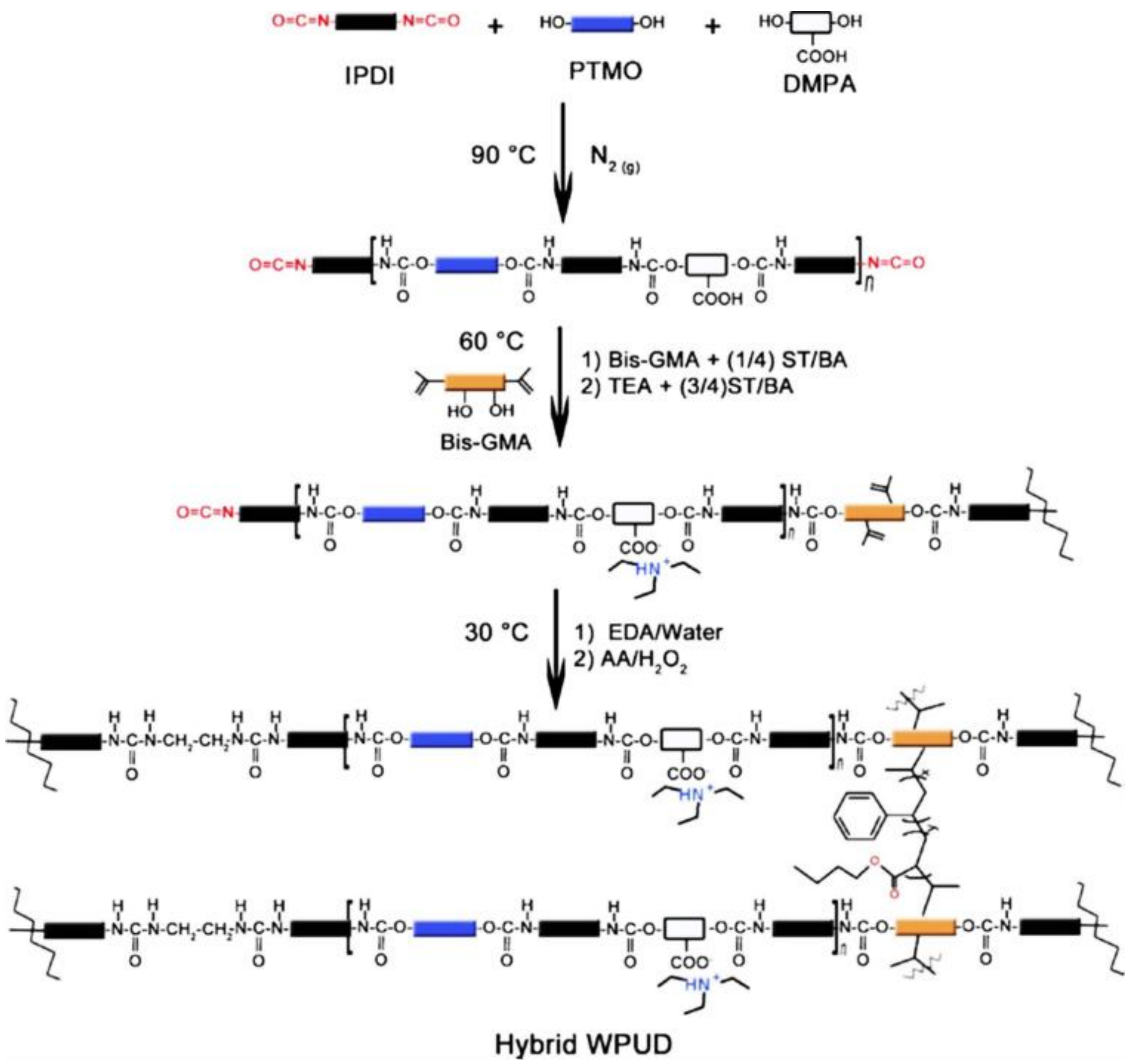

Figure 3. Scheme of the synthesis of WPUA dispersion chain extended without BD, with 50% of Bis-GMA and 50% EDA

In 2018 [25], Pardini and his colleagues developed pH-sensitive PU/DEA hybrid films, where 2-(diethylamino)ethyl methacrylate (DEA) and isophoronediisocyanate (PU)-based polyurethanes were used (Figure 4A). In particular, the DEA-rich system (50 wt.%) polymer films were able to adsorb Cu^{2+} and Zn^{2+} ions, with the highest removal efficiency observed at pH 4.0. The study showed that the systems preferred Cu^{2+} ions over Zn^{2+} ions, and the adsorption data were consistent with the Langmuir adsorption model. Deng and his colleagues developed water-based polyurethane-acrylate emulsions in 2018 [26], where they used isophoronediisocyanate, polytetramethylene glycol, and acrylate monomers. The study analyzed the effects of the NCO/OH ratio and the polyurethane/polyacrylic ratio (**Figure 4B**). As a result, the hybrid latex particles were spherical in shape and exhibited excellent stability. When using a 30/70 polyurethane/polyacrylic ratio, the hybrid coatings showed a loss factor of 0.3 or more at 75℃, which is particularly effective in reducing vibration.

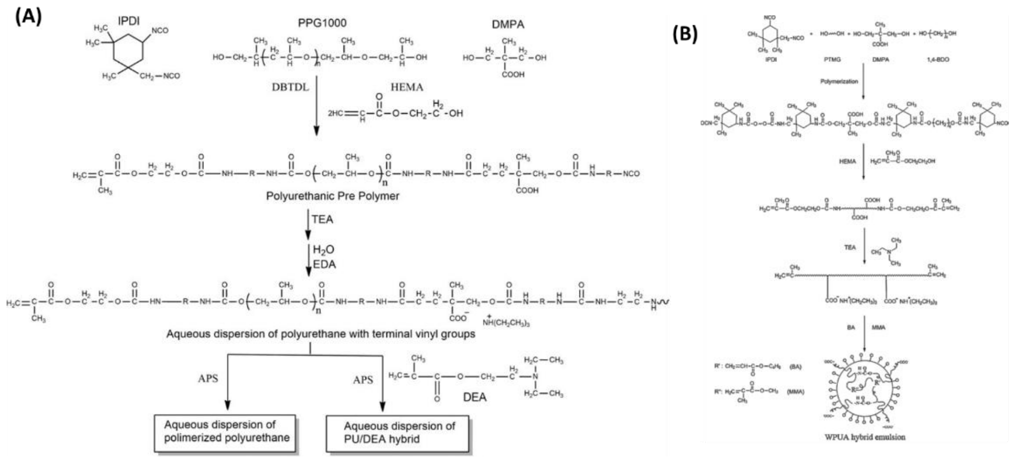

Figure 4. Synthesis of polymer dispersion.

In 2013 [27], Degrandi-Contreras and his team presented a technique for preparing urethane/acrylic hybrid latexes for pressure-activated adhesives using mini-emulsion polymerization. In this, isocyanate-terminated polyurethane is addition-polymerized with hydroxyl-rich acrylic material (HEMA) and free-radical polymerization of acrylic monomers occurs simultaneously. The amount of HEMA controls the rate of gel formation, crosslinking density, and the state of the polymer network. This microscopic structure was analyzed by Monte Carlo simulation, which revealed the potential for urethane/acrylic hybrids with improved shear resistance. In 2011[28], Lopez and his colleagues used a one-step mini-emulsion polymerization method to prepare water-based polyurethane-acrylic hybrid nanoparticles for pressure-activated adhesives. Adding polyurethane to it significantly increases the adhesive strength and shear holding time, making it an ideal alternative to high-performance adhesives. However, mixing methyl methacrylate causes phase separation and the formation of hemispherical structures, which reduces the tack strength. This study highlights the importance of the sensitivity of viscoelastic and adhesive properties to the structure of the polymer network. In 2019, [29] Mehravar and his colleagues prepared polyurethane/acrylic dispersions using a solvent-free method, analyzing the effect of phase composition on colloidal structure, polymer grafting, and mechanical properties of cast films. The dispersions showed a polyurethane shell/acrylic core structure, which formed a transformed structure and acted as a filler material. The use of high Tg copolymers resulted in films with strong mechanical properties. Grafting between the polyurethane and acrylic phases increased the compatibility but did not significantly change the mechanical properties. The study presents a strategy for preparing polyurethane/acrylic hybrids with controlled mechanical properties. Different amounts of hydroxyethoxypropyl-terminated compounds were added to the preparation of poly(siloxane-ether-urethane)-acrylic (PU-AC) hybrid emulsions.

In 2017 [30], Ye and his colleagues analyzed the effect of adding polydimethylsiloxane (PDMS) to the acrylic-terminated poly(ether-urethane) backbone (**Figure 4A**). The in situ copolymerization of methyl methacrylate and butyl acrylate was carried out by an emulsion method. The addition of PDMS resulted in larger particle size and lower viscosity. As a result, the films had increased flexibility, water repellency, and surface hydrophobicity, which could be useful in antifouling and surface coating. In 2015 [31], Ma and his team applied hybrid synthesis technology to prepare water-based polyurethane/acrylic hybrid emulsions. 2-Ethylhexyl acrylate increased the elasticity of the films, while N-acryloylmorpholine improved the high gloss, strength, and adhesion (Figure 4B). The combination of these two components produced hybrid films with intermediate properties. Increasing the proportion of N-acryloylmorpholine leads to qualitative changes in the emulsion and film, especially increasing gloss and increasing hydrogen bonding interactions.

In 2016, [32] Hailin and his team prepared and analyzed crosslinkable waterborne polyurethane (CWPU) and polyurethane-acrylic (CWPU/AC) hybrid emulsions using different ratios of trimethylolpropane (TMP) and acrylic monomer. The study evaluated the emulsion stability, particle size, viscosity, and mechanical and thermal properties of the films. XPS analysis showed that the silicon and fluorine-enriched films exhibited improved tensile strength, modulus, and hardness. The optimal addition of TMP and acrylic monomer (0.04 mol/50 wt%) revealed the potential for high-performance antifouling coatings. In 2014, [33] Zhang and his team combined polyacrylic ester (PA) and water-based polyurethane (PU) to prepare polyurethane-polyacrylic ester (PUPA) hybrid emulsions. The structure and chemical properties of these hybrid nanoparticles were evaluated (**Figure 4C**). While PUPA-C showed high moisture reactivity and preservation capacity, PUPA film exhibited improved hardness, high gloss, effective water resistance and tolerance to moisture absorption.

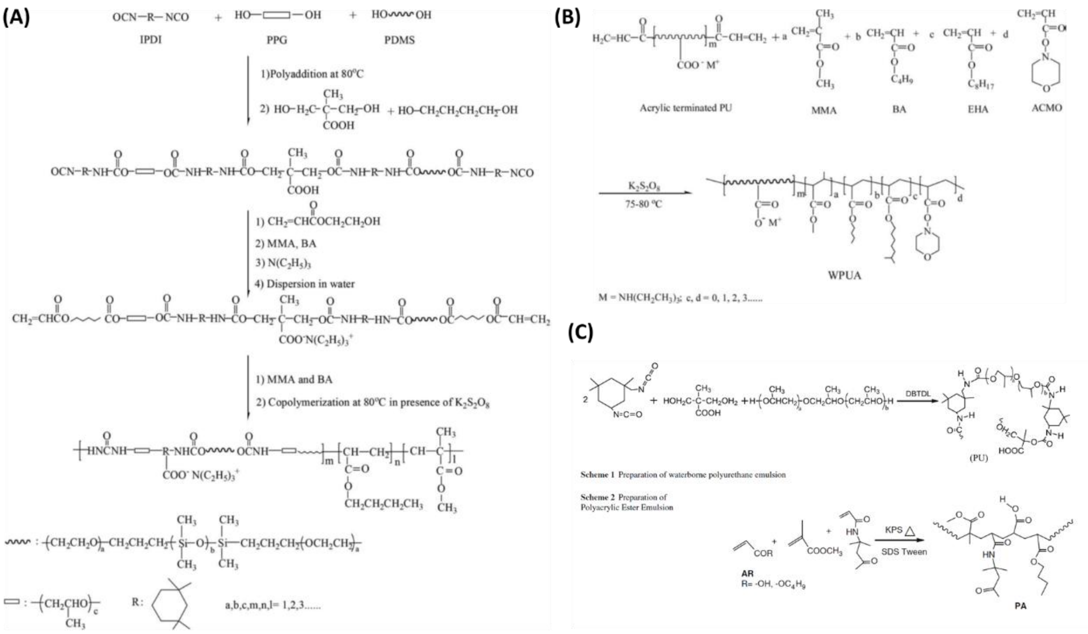

Figure 4. Synthesis scheme of PU-AC hybrid emulsion.

Mehravar et al. [34] (2019) have highlighted the importance of seeded emulsion polymerization for the synthesis of surfactant-free water-based PU/acrylic hybrids in a comprehensive analysis of PU/acrylic hybrid dispersions. The study shows that although PU dominates, it does not affect the incorporation of acrylic components with high glass transition temperatures (Tg). In addition, the need for further expansion of this study is highlighted due to environmental impacts and increasing regulatory policies. Yi et al. [35] (2017) prepared and analyzed high-performance PU-AC hybrid emulsions with different AC/PU weight ratios (45/55 to 70/30) using allyl polyoxyethylene ether (APEE). The study shows that core-shell structures are formed without cross-linking, and increasing the AC/PU ratio leads to an increase in particle size and a decrease in viscosity. The films exhibit improved mechanical properties, such as high water resistance, tensile strength and hardness. In addition, the type of acrylate component (MMA, BA or their mixture) plays a significant role in determining the performance of the emulsion. The study specifically focuses on the role of APEE in chemical crosslinking and the facile process for preparing hybrid emulsions with high AC/PU ratios.

Wu and his team [36] (2019) synthesized water-based polyurethane (WPU) using different concentrations of dimethylolpropionic acid (DMPA), which is used as a surfactant in soap-free emulsion copolymerization. This resulted in the formation of core-shell polyurethane/polyacrylate (PUA) composite emulsions. The study showed that the addition of WPU reduced the surface tension and increased the conversion rate of acrylic monomer by 98%. FTIR-ATR and TEM analysis confirmed the presence of the core-shell structure and the improvement of the WPU-PUA compatibility. In addition, increasing the DMPA content increased the strength and toughness of the PUA film. Xu and his colleagues [37] (2021) developed CO2-controlled water-based polyurethane-acrylate (WPUA) to overcome the limited water resistance of conventional WPU, to which methyl methacrylate (MMA) units were attached. The study shows that WPUA enriched with MMA at 10% weight ratio exhibits improved mechanical properties, such as high tensile strength (16.7 MPa) and modulus (85.9 MPa) (Figure 5). It also showed improved water resistance with only 2.15% water absorption and 0.17 L linear swelling ratio. The study highlights the stable dispersion and high performance of CO2-activated WPUA latex particles.

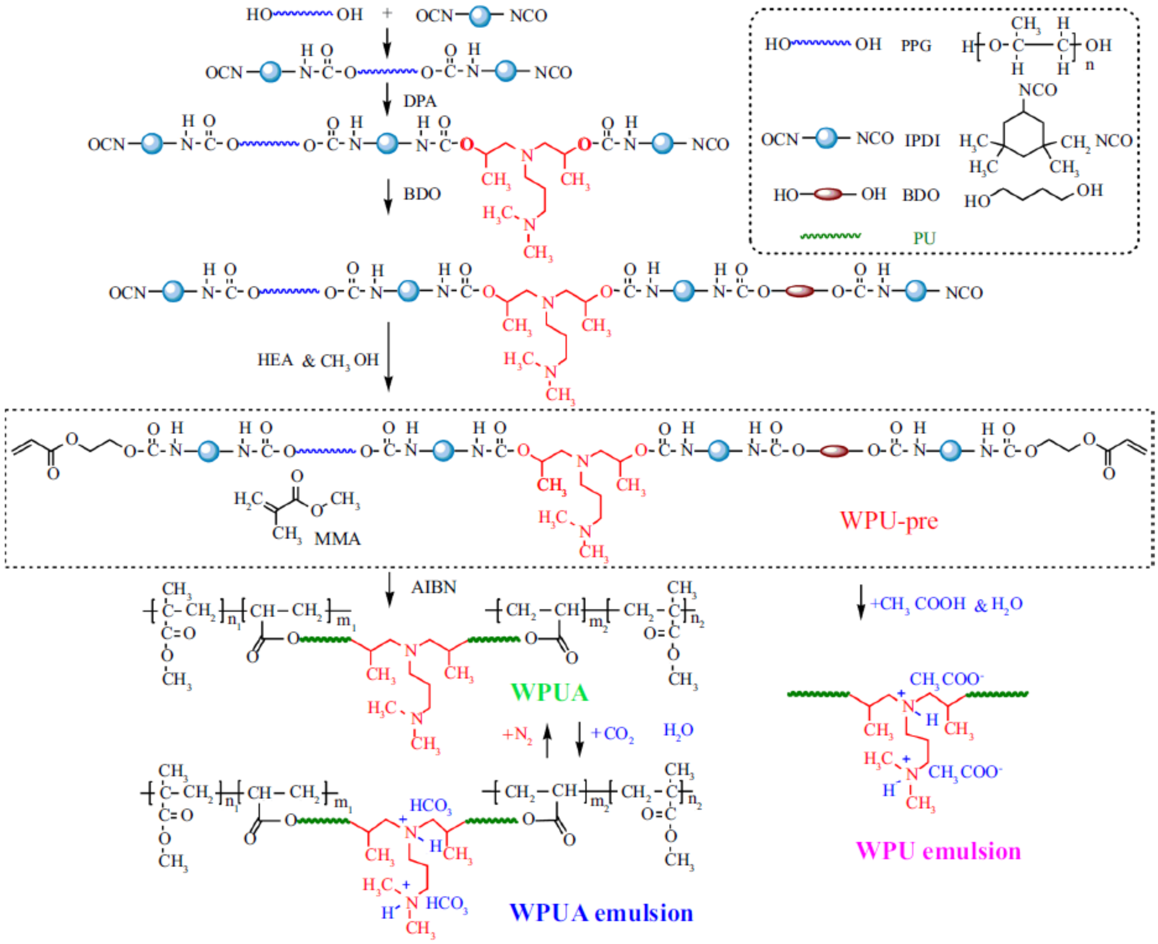

Figure 5.Synthetic procedure of WPU and WPUA emulsions.

In 2017 [38], Ma and his team developed water-based polyurethane-acrylate (WPUA), where WPUA was polymerized as a seed emulsion and then methyl methacrylate (MMA) and butyl acrylate (BA) were added. The researchers controlled the concentration of polyacrylate (PA) in WPU by using poly(propylene carbonate) (PPC) diol as a softening agent. According to the results, the adhesion, hardness, water resistance and hydrophilicity of WPUA films were significantly improved, indicating excellent compatibility and mutual influence between PPC-based WPU and PA. This improved the thermal stability and performance of the coating. In 2018, [39] Maurya and his colleagues published a review on polyurethane-acrylate (PUA) oligomers, which discussed in detail the structure, modification, curing process and mechanical, optical and thermal properties of a new type of PUA prepared by capping polyols with diisocyanates and acrylates. The study emphasizes the need for new modifications to improve the performance of PUA and notes that current advances in PUA chemistry have created opportunities for the development of customized formulations tailored to specific applications.

In 2018 [40], Jiang and his team developed water-based polyurethane (WPU) modified with acrylate and nano-zinc oxide (ZnO) (PUA/ZnO) to improve the wet abrasion resistance of dyed cotton fabrics. The abrasion resistance of the processed fabrics increased by 0.5-1 order of magnitude, ultimately achieving a rating of 3-4. In addition, the fabrics exhibited improved UV protection of 50+ UPF level. SEM analysis showed a smooth and uniform coating on the fabric surface, which reduced abrasion and improved toughness. In 2013 [41], Shi and his team prepared TDI-polyurethane/polyacrylate (TDI-PU/PA) composite emulsions using methyl methacrylate (MMA) and butyl acrylate (BA) in a solvent-free method. This synthesis uses TDI, polypropylene glycol (PPG), 1,6-hexanediol (HDO) and dimethylol propionic acid (DMPA), which produces latex films exhibiting improved tensile strength and stiffness (Figure 6). The addition of MMA significantly increases water resistance and TDI-PU/PA is more cost-effective, exhibits higher dye retention, improved film stiffness and strong coating ability compared to IPDI-PU/PA.

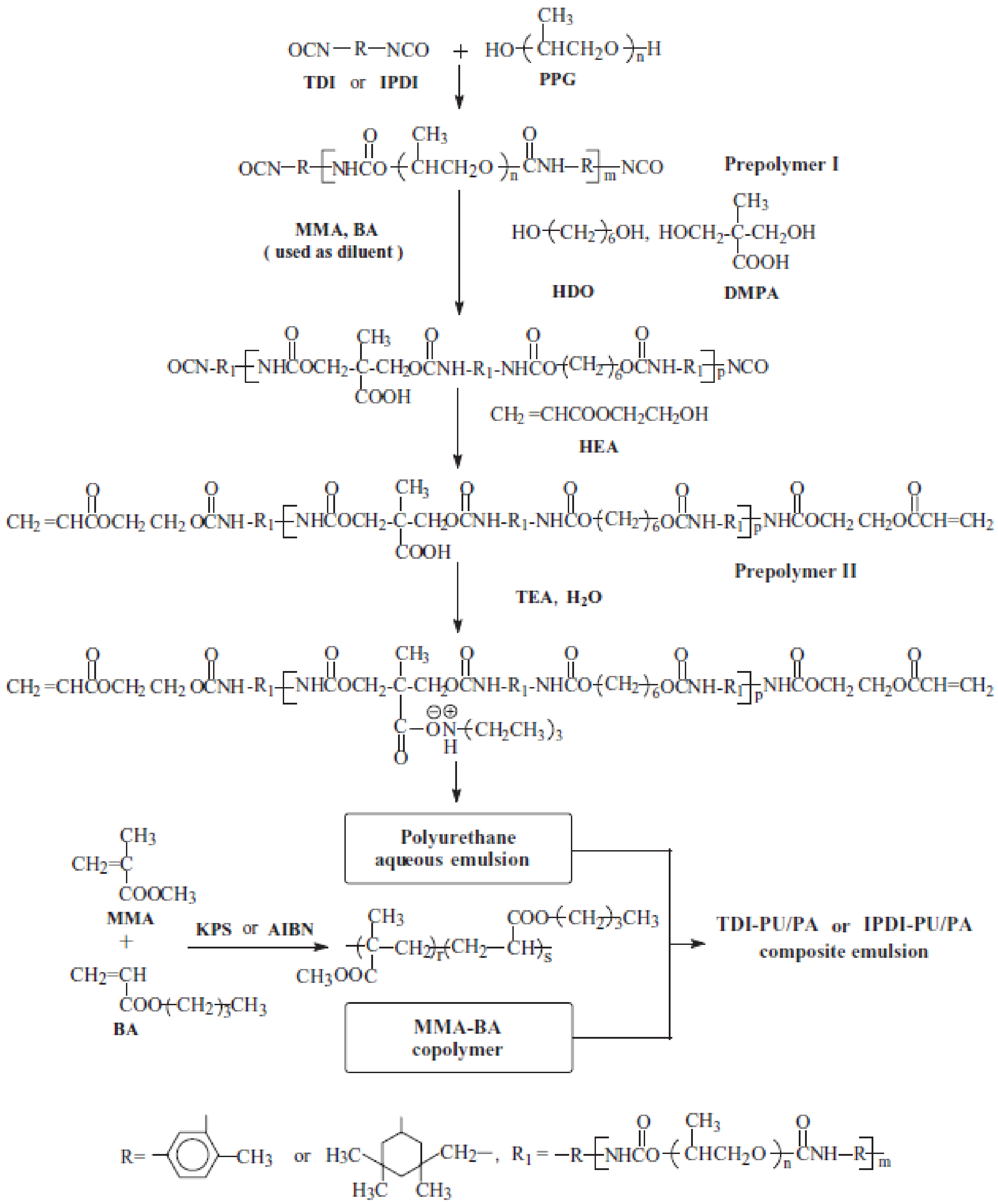

Figure 6. Preparation process of TDI-PU/PA and IPDI-PU/PA composite emulsions.

II. Conclusion:

Polyurethane hybrids have found important applications in various industries. Mostly, hybrid binders prepared from a combination of polyurethane and acrylic have gained special importance in the coatings industry due to their unique properties. These materials have shown significant potential in coatings, two-part coatings, adhesives, and pressure-sensitive materials. Further research in this area may be helpful in developing new combinations and improving properties for specific applications.

III. Acknowledgments:

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