YALOVA UNIVERSITY ★ GRADUATE SCHOOL of SCIENCE ENGINEERING and TECHNOLOGY

PREPARATION OF WATER BORNE ANIONIC POLYURETHANE AND ACRYLATE GRAFTED POLYURETHANE DISPERSIONS FOR COATING APPLICATIONS ON TEXTILE SUBSTRATES

M.Sc. THESIS

Öznur EMEKLİOĞLU

Department of Polymer Engineering

Polymer Engineering Programme

Thesis Advisor: Assoc. Prof. Dr. Emine Hilal MERT

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YALOVA ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

TEKSTİL SUBSTRATLARI ÜZERİNE KAPLAMA UYGULAMALARI İÇİN SU ESASLI ANYONİK POLİÜRETAN VE AKRİLAT AŞILANMIŞ POLİÜRETAN DİSPERSİYONLARININ HAZIRLANMASI

YÜKSEK LİSANS TEZİ

Öznur EMEKLİOĞLU
(125101011)

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Tez Danışmanı: Doç. Dr. Emine Hilal MERT

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Öznur Emeklioğlu, a **M.Sc.** student of YALOVA **Institute of Science and Engineering** student ID **125101011**, successfully defended the **thesis** entitled “**PREPARATION OF WATER BORNE ANIONIC POLYURETHANE AND ACRYLATE GRAFTED POLYURETHANE DISPERSIONS FOR COATING APPLICATIONS ON TEXTILE SUBSTRATES**”, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Assoc. Prof. Dr. Emine Hilal MERT**
Yalova University

Jury Members : **Assist. Prof. Dr. Yasemin TAMER**
Yalova University

Assist. Prof. Dr. İlke ANAÇ
Gebze Technical University

Assoc. Prof. Dr. Emine Hilal MERT
Yalova University

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To my beloved daughter,

FOREWORD

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December 2018

Öznur EMEKLİOĞLU
(Mother and Chemist)

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ABBREVIATIONS

Ac : Acrylate
AAS salt : 2-[(2-aminoethyl)amino]ethanesulfonic Acid Sodium Salt
APS : Ammonium Persulfate
BA : Butyl Acrylate
BDO : 1,4- butanediol
BES salt : N,N-bis(2-hydroxyethyl)-2-aminoethane sulfonic acid sodium salt
BuMA : Butyl Methacrylate
DBTDL : Dibutyltin Dilaurate
ΔBS : Delta Back Scattering
DMBA : 2,2-bis(hydroxymethyl)Butyric Acid
DMPA : Dimethylol Propanoic Acid
DSC : Differential Scanning Calorimetry
EA : Ethyl Acrylate
EHMA : 2-Ethyl Hexyl Methacrylate
FTIR : Fourier Transform Infrared Spectroscopy
HDI : Hexamethylene Diisocyanate
HEA : 2-Hydroxy Ethyl Acrylate
H_{12}MDI : Hydrogenated MDI
IPA : Isopropyl Alcohol
IPDI : Isophorone Diisocyanate
MEHQ : Monomethyl Ether Hydroquinone
MDI : 4,4'- Diphenyl Methane Diisocyanate
MMA : Methyl Methacrylate
NMP : N-Methyl Pyrolidone
PES : Polyester Polyol
PU : Polyurethane
PU/Ac : Polyurethane Acrylate
PUD : Polyurethane Dispersion
SDS : Sodium Dodecyl Sulfate

TDI	**:** 2,4- or 2,6-Toluene Diisocyanate
Tg	**:** Glass Transition Temperature

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PREPARATION OF WATER BORNE ANIONIC POLYURETHANE AND ACRYLATE GRAFTED POLYURETHANE DISPERSIONS FOR COATING APPLICATIONS ON TEXTILE SUBSTRATES

SUMMARY

Aqueous polyurethane dispersions (PUDs) provide excellent impact and abrasion resistance to the materials by forming films on their surface. For this reason, they have wide range of applications in textile, adhesive, and wood coating industries. Aqueous PUDs are defined as binary colloidal systems in which the PU particles are dispersed in a continuous aqueous medium. However, in order to disperse water immiscible PU polymer chains in water, ionic and/or nonionic hydrophilic segments should be associated with the conventional PU structure. Therefore, PUDs are generally prepared by dispersing isocyanate terminated PU prepolymers, in the aqueous systems consisting of colloidal stabilizers. Preparing hybrid PU/polyacrylate (PAc) colloidal systems by mixing aqueous PUDs with polyacrylates (PAc), on the other hand, could be a favourable approach for the improvement of mechanical and chemical resistance of the coating materials. However, poor compatibility between PAc and PU components could cause the loss of film properties most of the time. In such case, chemical bonding between PU and PAc chains could be used as a versatile approach for obtaining hybrid systems exhibiting excellent properties of both kinds.

With this thesis, by using aliphatic isocyanates and difunctional polyesters, solvent-free PUDs having 25-30% of solid content were prepared through acetone process. Afterwards, in order to introduce vinyl functionality, resulting PU prepolymers were reacted with a hydroxyl functional acrylate monomer. Then PAc grafting on the PU chains was achieved by seeded emulsion polymerization between the vinyl functional PU chains and acrylate monomers. Additionally an acylate emulsion was obtained via emulsion polymerization of butylacrylate (BA), ethylacrylate (EA) and hydroxyetyl acrylate (HEA) in order to characterize hybrids more accuretly.

Chemical structures of the resulting materials were characterized by Fourier Transform Infrared (FTIR) spectroscopy. Moreover, solid content, pH, viscosity, particle size distribution, and stability of the resulting dispersions were also studied. On the other hand, thermal properties of the films prepared from the obtained dispersions were also investigated by using Diferantial Scanning Caloremetry (DSC), while mechanical properites were determined in terms of Shore A hardness and tensile strength. In the end, application properties of resulting materials in textile industry were examined by investigating the final properties of coated textile substrates.

TEKSTİL SUBSTRATLARI ÜZERİNE KAPLAMA UYGULAMALARI İÇİN SU ESASLI ANYONİK POLİÜRETAN VE AKRİLAT AŞILANMIŞ POLİÜRETAN DİSPERSİYONLARININ HAZIRLANMASI

ÖZET

Kaplama teknolojisinde kullanılan sulu poliüretan dispersiyonlar (PUD'lar), malzeme üzerinde oluşturdukları filmler sayesinde malzemeye mükemmel elastikiyet ve abrazyon dayanımı ile düşük sıcaklıkta yüksek darbe dayanımı kazandırırlar. Bu nedenle de tekstil, plastik ve odun esaslı çeşitli ürünlerde yapıştırıcı veya kaplama malzemesi olarak yaygın bir kullanım alanına sahiptirler. Sulu poliüretan dispersiyonlarının yanı sıra akrilik reçineler de kaplama sanayisinde önemli bir ticari kullanım alanına sahiptir. Diğer yandan, sulu poliüretan dispersiyonlarının (PUD'ların) poliakrilatlar (PAc'ler) ile karıştırılmasıyla elde edilen özgün sistemler ile hem kaplama malzemelerinin mekanik mukavemeti hem de çözücü ve kimyasallara karşı olan dayanımları geliştirilebilmektedir. Ayrıca bu türden uygulamalar ile önemli bir ekonomik kazanç da sağlanabilmektedir. Buna rağmen, PAc'ler ile PU bileşenleri arasındaki düşük uyum film özelliklerinin kaybına neden olabilmektedir. Ancak, PU ve PAc polimerlerinin kimyasal bağlarla bağlanması ile elde edilen melez yapılar, bileşenlerin uyumluluğunu arttırarak her iki türün özelliklerini de barındıran mükemmel sistemlerin oluşumuna olanak vermektedir.

Bu kapsamda sunulan tez çalışması ile, tekstil malzemelerinin kaplanmasında kullanılmak üzere 3 farklı emülsiyon geliştirilmiştir. İlk olarak konvensiyonel emülsiyon polimerizasyon yöntemiyle butil akrilat (BA), etil akrilat (EA) ve hidroksietil akrilat (HEA) monomerleri kullanılarak ağırlıkça 25-30% oranında kuru maddeye sahip bir emülsiyon hazırlanmıştır. İkinci adımda ise, ağırlıkça 25-30% oranında kuru maddeye sahip anyonik PUD'lar aseton prosesi kullanılarak sentezlenmiştir. Anyonik PUD'ların sentezi hekzametilen diizosiyanat (HDI), farklı molekül ağırlıklarına sahip poliester dioller (Mw: 1000 g/mol, Mw: 2000 g/mol ve Mw: 3000 g/mol), iyonomer ve zincir uzatıcı ajan (2-[(2-aminoetil)amino]ethansülfonik asit sodyum tuzu) kullanılarak gerçekleştirilmiştir.

Formülasyonlar geliştirilirken, NCO/OH oranı ve zincir uzatıcı iyonomer miktarı değiştirilerek PUD yapısı ve özellikleri üzerinde belirleyici olduğu bilinen iki temel faktörün etkisi araştırılmıştır. Bu amaçla, ilk olarak NCO/OH oranı 1.5 olarak sabit tutularak 3 adet formülasyon geliştirilmiş ve dispersiyonlar sentezlenmiştir. Ardından bu oran 2 olarak sabit tutularak 3 farklı formülasyon daha geliştirilmiş ve bu formülasyonlar ile 3 yeni dispersiyon elde edilmiştir. Daha sonraki aşamada ise 3000 g/mol molekül ağırlığına sahip poliester diol ve HDI kullanılarak geliştirilen formülasyonlarda NCO/OH oranı 2 olarak sabit tutularak zincir uzatıcı miktarı arttırılmış ve geliştilen bu formülasyonlar üzerinden 2 yeni dispersiyonun daha sentezi gerçekleştirilmiştir.

Tezin üçüncü aşamasında ağırlıkça 25-30% oranında kuru maddeye sahip poliüretan akrilat (PU/Ac) hibrit dispersiyonları hazırlanmıştır. Bu amaçla, öncelikle tezin ikinci aşamasında sentezlenen 8 adet dispersiyondan elde edilen filmlerin mekanik özellikleri incelenmiş ve en sert özellik gösteren formülasyon seçilmiştir. Ardından, seçilen anyonik PUD reçetesi baz alınarak ve emülsiyon polimerizasyonunda kullanılan BA ve EA oranları sabit tutularak, hazırlanan monomer karışımının toplam miktarının sırasıyla 5% ve 10% oranında arttırılması ile 2 farklı formülasyon elde edilmiştir. Akrilat monomerlerinin PU zinciri üzerine aşılanması çekirdekli emülsiyon polimerizasyonu ile gerçekleştirilmiştir. PU prepolimerine vinil grubu fonksiyonalitesi kazandırmak için ise HEA monomeri kullanılmıştır. Bu amaçla, öncelikle serbest NCO uç gruplarına sahip PU prepolimeri sentezlenmiş, ardından kalan serbest NCO grupları ile zincir uzatıcı iyonomer ve HEA aseton prosesi kullanılarak reaksiyona sokulmuştur. Daha sonra hibrit dispersiyonlar, konvensiyonel çekirdekli emülsiyon polimerizasyonu ile, HEA birimleri takılarak vinil fonksiyonalitesi kazandırılan PU prepolimeri üzerine BA ve EA’dan oluşan monomer karışımının farklı oranlarda katılması ile hazırlanmıştır.

Elde edilen emülsiyon ve dispersiyonlar fizikokimyasal özelliklerinin ve kararlılık davranışlarının incelenmesi ile karakterize edilmiştir. Bu kapsamda öncelikle Fourier Transform Infrared (FTIR) spektroskopisi ile kimyasal yapı tayini yapılmıştır. Ardından sentezlenen malzemelerin kuru madde miktarı, pH’si, viskozitesi ve partikül boyutu belirlenmiştir. Sentezlenen dispersiyonların 40°C’deki kararlılık analizi Turbiscan Lab cihazı kullanılarak gerçekleştirilmiştir. Fizikokimyasal özellikleri ve kararlılık durumu belirlenen dispersiyonların filmleri öncelikle 2 gün süre ile oda sıcaklığında ve ardından yine 2 gün süre ile 70 °C deki hava sirkülasyonlu etüvde bekletilerek oluşturulmuştur. Elde edilen filmlerin ısıl özellikleri Diferansiyel Taramalı Kalorimetre (DSC) cihazı ile araştırılmıştır; mekanik özellikleri ise Shore A sertliklerinin ve 1 kN yük altındaki çekme dayanımı özelliklerinin ölçülmesi ile karakterize edilmiştir.

Elde edilen dispersiyonların tekstil kumaşlarına kazandırdıkları özellikler kumaş üzerine kaplama yoluyla araştırılmıştır. Bu amaçla hazırlanan dispersiyonlar öncelikle akrilat bazlı bir sentetik kıvamlaştırıcı ile aynı viskoziteye (~5000 mPas) sahip olacak şekilde kıvamlaştırılmış, ardından üzerlerine pastaların uygulandığı kumaşlar laboratuar ölçekli ramlar içerisinde kurutulmuş ve fikselenmiştir. Daha sonra, bıçak havada kaplama yöntemi kullanılarak hem siyah renkli 100% pamuk dokuma kumaşa pasta halinde, hem de beyaz renkli 100% pamuk dokuma kumaşa kırmızı pigment boyar madde içeren pasta halinde kaplanmış ve kaplanan kumaşlar görsel olarak parlaklık yönünden, dokunsal olarak yumuşaklık ve yıkama dayanımları yönünden incelenmiştir. Pigment bağlama özellikleri ise hem renk derinliği, hem kuru-yaş sürtme haslıkları, hem de yıkama dayanımlarına bakılarak kontrol edilmiştir.

Yapılan çalışmalar sonucunda, hazırlanan PUD’ların NCO/OH oranının, zincir uzatıcı iyonomer miktarının ve kullanılan poliolün molekül ağırlığının fizikokimyasal özellikleri, emülsiyon kararlılığı, dispersiyonlardan hazırlanan filmlerin ısıl ve mekanik özellikleri ve kaplanan kumaşlar üzerindeki yumuşaklık, parlaklık ve kırmızı pigment bağlama özellikleri üzerindeki etkileri tartışılmıştır. Sonuç olarak; elde edilen PUD’ların partikül büyüklüğü dağılımının NCO/OH oranı, kullanılan poliollerin molekül ağırlığı, zincir uzatıcı ajan miktarı ve akrilat içeriğine bağlı olarak değiştiği saptanmıştır. Bu kapsamda, kullanılan poliolün molekül ağırlığının ve zincir uzatıcı ajan miktarının artmasıyla ve NCO/OH oranının düşmesiyle PUD’ların partikül boyutunun daha düzenli dağılım gösterdiği belirlenmiştir. Bununla birlikte, akrilat

içeriğindeki artışın da partikül boyutunun daha düzenli bir dağılım sergilemesinde etkili olduğu gözlemlenmiştir. Turbiscan Lab cihazı kullanılarak gerçekleştirilen kararlılık analizi sonuçlarının karşılaştırılması ile de NCO/OH oranının, poliollerin molekül ağırlığının ve zincir uzatıcı ajan miktarının ve akrilat içeriğinin kararlılık üzerinde önemli bir etkiye sahip olduğu tespit edilmiştir: PUD'ların kararlılığının poliolün molekül ağırlığının ve zincir uzatıcı ajanın miktarının artması ile ve NCO/OH oranının azalması ile azaldığı sonucuna varılmıştır. Ayrıca, PU zincirine akrilat monomerlerinin aşılanmasının da ürün kararlılığını azalttığı gözlemlenmiştir.

Elde edilen dispersiyonların ısıl özelliklerinin karakterizasyonu sonucunda, bütün ürünlerde düşük sıcaklıkta ortaya çıkan ve yumuşak segmentten geldiği değerlendirilen tek camsı geçiş sıcaklığı (Tg) geçişi gözlemlenmiş, bununla birlikte herhangi bir kristallenme ya da erime piki gözlemlenmemiştir. Buna ek olarak, eşit NCO/OH oranına sahip PUD'ların karşılaştırılması sonucunda yumuşak segmentin Tg'sinin kullanılan poliolün molekül ağırlığı arttıkça ve sert segment içeriği azaldıkça azaldığı saptanmıştır. Ayrıca, aynı molekül ağırlığına sahip polioller kullanılarak hazırlanan PUD'lar için Tg değişiminin NCO/OH oranından bağımsız olduğu belirlenmişitr. PU/Ac hibrit dispersiyonların Tg değerlerinin akrilat içeriğinin artmasıyla birlikte, beklenildiği üzere, PAc emülsiyonundan elde edilen filmin Tg değerine yaklaştığıtespit edilmiştir.

Sentezlenen malzemelerden hazırlanan filmlerin Shore A sertlik değerlerinin karşılaştırılması sonucunda kullanılan poliolün molekül ağırlığının ve akrilat içeriğinin artmasıyla filmlerin yumuşaklığının arttığı gözlemlenmiştir. Çekme testi sonuçlarının karşılaştırılması sonucunda ise poliolün molekül ağırlığının artmasıyla numunelerin kopma uzaması değerlerini arttırtığı ancak gerilme mukavemetlerinin azaldığı belirlenmiştir. Tüm bunlara ek olarak, akrilat aşılama ile sentezlenen hibrit yapılarda, PU yapısına akrilat zincirlerinin katkısının gerilme mukavemetinin azalmasına neden olurken kopma uzamasını arttırdığı bulunmuştur. Ayrıca, akrilat içeriğinin artmasının da gerilme mukavemetinde ve kopma uzamasında daha fazla azalmaya yol açtığı belirlenmiştir.

Sentezlenen malzemelerin tekstil uygulaması sonuçlarının karşılaştırılması sonucunda, genel olarak tüm malzemelerin kumaşın yumuşaklık ve parlaklık özelliklerine katkı sağladığı gözlemlenmiştir. Ancak, kullanılan poliolün molekül ağırlığının ve NCO/OH oranının artmasıyla bu özelliklerin daha belirgin olarak iyileştiği saptanmıştır. Bununla birlikte, PU zincirine aşılanan akrilat içeriğinin artması ile yumuşaklığın arttığı ve parlaklığın azaldığı bulunmuştur. Ayrıca, akrilat emülsiyonu ve hibrit dispersiyonlar ile kaplanan kumaşların yıkama dayanımlarının, endüstriyel uygulamalar için yeterli olduğu sonucuna varılmıştır. Tüm bunlara ek olarak, Data color cihazı ile gerçekleştirilen ölçüm sonuçlarına dayanılarak kumaş renginin koyuluğunun, kullanılan poliolün molekül ağırlığı ve NCO/OH oranının artmasıyla ve iyonik merkezin azalmasıyla arttığı sonucuna varılmıştır. Ayrıca, PU omurgasına akrilik segmentin aşılanmasının kumaşlarda daha koyu bir görünüme neden olduğu bulunmuştur. Öte yandan, NCO/OH oranının ve PU omurgasındaki iyonik merkezin artmasının ve kullanılan poliolün molekül ağırlığının azalmasının kumaşlarda yıkama sonrası renk kaybını arttırdığı gözlemlenmiştir. Ayrıca, PU omurgasına akrilik segment aşılananması ile kumaşların bir yıkamadan sonraki renk tutma özelliğinin iyileştiği saptanmıştır. Diğer yandan, pigment kaplı kumaşların kuru sürtünme haslıklarının NCO/OH oranının artmasıyla arttığı ve PU omurgasına daha fazla iyonik merkez ve akrilat segmenti eklenmesiyle azaldığı bulunmuştur. Ayrıca, sentezlenen PUD'ların yaş sürtme haslıklarının genel olarak zayıf olduğu, ancak akrilat içeriğinin artmasıyla bu özelliğin geliştiği belirlenmiştir.

1. INTRODUCTION

Waterborne dispersions are environmentally safe to be used and have improved properties and application performance characteristics compared to solventborne dispersions, industries including paint, coatings, adhesives use them more widely over the past several decades instead of their solventborne types. Polyurethanes and polyacrylates are most popular chemistries used in waterborne dispersions for coating systems. Specifically acrylic dispersions have been largely used in architectural coatings since 1950s, acrylic polymers were introduced as binders [1-5].

Acrylic based resins generally show good adhesion behaviour and excellent performance in all weather conditions. Besides that, they have affinity to pigments and other ingredients. Moreover, having relatively low cost and well understood structure-property relationships are their other important characteristics [6]. Due to their generally showing low glass transition temperature (Tg), they can be easily handled, processed and used in variety conditions. Additionally, physical properties of final polymeric resin can be adjusted within possibility of using large and various range of available monomers in the market. However, number of techniques, for crosslinking polymer chains, have been developed to improve their limited thermal stability and mechanical strenght due to their flexible backbones [7].

Another unique class of poymers is polyurethanes (PUs). Since their properties can be finely tuned by changing their components, PUs have a broad range of applications [8]. Their special and versatile properties, including chemical, solvent, abrasion resistance, flexibility, gloss and toughness, give them both technical and economic importance. Exclusively replacing their solventborne types, today waterborne PUs started to be used in new application areas as coating materials, adhesives, additives for paints, dyes, defoamers, associate thickeners, caulking materials [9–21]. Furthermore, because of their excellent physcial and mechanical properties, aqueous polyurethane dispersions (PUD) have a growing attention leading them to be used in a wide range of applications [22–24]. Excellent film forming properties are resulted from being a block copolymer including soft segments which can have Tg value down to – 60 °C [25]. In order to alter their film forming ability and consistency with other polymers, the ratio of monomers and structure between hydrophobic and hyrophilic groups can be simply adjusted [26].

There are many literatures reporting the preparation methods and relationships of structure and properties of polyurethane-acrylic (PU/Ac) hybrid dispersions in which polyacrylate molecule is introduced in polyurethane molecule resulting in formation of synergistic effect of polyacrylate and PU [27–29].

Besides their significant advantages, acrylics have some disadvantages such as limited chemical stability and mechanical properties and PUs have some disadvantages such as high cost, low pH stability and fair outdoor durability.There is a suprising fact that synergistic effect of polyacrylate and PU may cause their disadvantages′ elimination mutually [30]. Within the purpose of enhancing the properties of both acrylics and PUs and obtaing effective lower cost products, researchers and end-use applicators have been focusing on combination of them. It is now definitely known that direct formulation of waterborne dispersions is the best simple way to benefit from their synergistic properties [31-34].

However, compatibility between acrylic and polyurethane is limited and this could lead to stability problem such as cloudiness/haze and reduction in gloss in dried films and sedimentation or viscosity increase on storage after making formulation.Therefore, preparation of hybrid type of emulsion is an alternative approach. In contrast with physical formulations, having seperated acrylic and PU moeities, there occurs a molecular level combination of urethane and acrylic polymers in single component hybrids resulting in excellent balance of properties of both types [35].

According to literature research for preparation of waterborne PUDs, acetone method and prepolymer mixing method were studied and compared with respect to their effects on final properties and structures of resulting dispersions by Pérez-Limiñana et al. [36]. Anionic waterborne polyurethanes synthesized by using different two ionic centers with dimethylol propionic acid (DMPA) and N,N-bis(2-hydroxyethyl)-2-aminoethane sulfonic cid sodium salt (BES salt), poly(ε-caprolactone), hydrogenated MDI (H12MDI) and 1,4- butanediol (BDO) were compared with respect to their effects on the mechanical properties, thermal stability, glass transition temperature (Tg), particle size distribution and viscosity of prepared emulsions by Honarkar et al [37]. Another type of waterborne PU was prepared by Ma et al. using both 2,2-bis(hydroxymethyl)butyric acid (DMBA) and 2-[(2-aminoethyl) amino]-ethanesulfonic acid monosodium salt (AAS salt) in the structure. On the other hand, Wu et al. were also studied waterborne PUs by using both AAS salt and liquefiable DMPA in the structure [38,39]. Regarding hybrid dispersions, several waterborne polyurethane–acrylates (PUA) were prepared based on PUs synthesized by using DMPA as ionic center and HEMA or HEA as end-capping agent and further polymerized with acrylate monomers like butyl acrylate (BuAc), styrene, methyl methacrylate (MMA) [40-46].

Related to textile applications of these materials, there are few publications reported in the literature. Series of PUDs synthesized by using DMBA, and mixtures of amphiphilic and hydrophobic polyols were investigated for their waterproof fabric coating applications [47]. Recently, another different type of PUD synthesized by using DMPA and chitosan were applied on fabrics by using pad-dry-cure technique and physical and antimicrobial properties of treated fabrics were evaluated [48,49]. Moreover, flame retardant properties of waterborne PUs synthesized by using a phosphorous based polyester polyol and isophorone diisocyanate (IPDI) in different mole ratios of NCO:OH were also studied [50]. Fabrics treated with different concentrations of polyurethane acrylate (PUAc) copolymers via dip padding techniques were evaluated with respect to their pilling and antimicrobial behaviours [44-46]. Besides that, non ionic types of PUAc's were studied as aqueous binders for pigment printing of all types of fabrics [51,52,54,55]. Additionally some commercially available PUDs and acrylate emulsions were investigated for their pigment binding abilities in literature [53,56-58].

In this thesis, anionic waterborne PUDs were prepared by using an ionomer having sulfonate groups (AAS salt) via acetone process. Then, the hybrid dispersions were obtained via further copolymerization reaction with butyl acrylate (BA) and ethyl acrylate (EA). For this purpose, pre-synthesized polyurethanes were first reacted with an end capping agent, hydroxyl ethyl acrylate (HEA), in order to gain double bond functioanility to the PU chains, and then different ratios of butyl acrylate (BA) and ethyl acrylate (EA) were added into the reaction mixture. In addition to PUDs and PUAc's, an acrylate emulsion was also prepared by using HEA, BA and EA, in order to make a comparision between the final product properties. For the evaluation of the influence of resulting emulsion and dispersions, all the materials were applied as paste via knife air coating on black woven cotton fabric. In order to examine their softness and glossiness and their pigment binding properties and as well as for determination of their possible usage as a future pigment printing or dyeing binder all the materials were applied as red pigmented paste via knife air coating on white woven cotton fabric. It is important to point out that AAS salt ionic center has not been studied in polyurethane acrylate hybrid dispersions using HEA, BA and EA acrylate monomers. Furthermore, fabric coating properties of these hybrids have not been investigated before.

2. THEORETICAL PART

2.1 Waterborne Polyurethane Dispersions (PUDs)

Aqueous polyurethanes, in which polyurethane particles including different chemical species are dispersed in water. Properties of final dispersions are changed due to their colloidal properties, interfacial forces or physicochemical interactions [59-60]. Stable colloidal dispersions are obtained via the uniform distribution of the discontinuous droplet phase in the continuous liquid medium. However, in some cases unstable dispersions are also formed when a single bigger droplet is formed by diffusion of droplets in each other. This process in which dispersed colloidal particles are agglomerated results in decrement of total surface area and called as coalescence or an aggregation. If a new particle is not produced but the particle size increases from submicroscopic microfloc to visible suspended particles then this process is called floculation. However, collision of microfloc particles faciliate agglomeration and produce larger flocules. In many studies, the effect of polymer in stabilization or flocculation of colloidal dispersion was investigated [59-63].

Waterborne PU is formed by a linear thermoplastic PU having ionic groups in its structure (i.e. a polyurethane ionomer). This ionic groups acts as an internal emulsifier and make polyurethane particles to be dispersible in water. There could be three kinds of ionic groups, which are cationic (quaternary ammonium groups), anionic (carboxylated or sulfonated groups), or non-ionic (polyols with ethylene oxide end groups). The ability of dispersing polyurethane particles in water and obtain stable dispersions are resulted from ionic groups in the ionomer.

Formation of small spheres bearing a core of aggregate hydrophobic segment and a boundary layer holding ionic groups leads the stabilization effect of ionic sites in water resulting in aqueous dispersion [64]. Anionic groups containing carboxylic acids and sulfonic acid groups are most commonly used among all ionic groups. Acid groups prevented of potential reaction with isocyanate as a result of steric hindrance are neutralized by using basic like tertiary amines. The properties of the dispersions are also affected by the choice of neutralizing agent. Fine particle sized PUDs are obtained from anionic groups, which are very stable dispersions. Mechanical and chemical properties of the films formed from these dispersions are better with comparison to other dispersions [65].

Cationic PUs are prepared by reacting isocyanate terminated prepolymers with water soluble ionic groups containing tertiary amines, quaternized with protonic acid or alkylating agent, called as cationomers. Within exception of some special applications, cationic PUs generally have lesser importance because of their application properties. However, since there are variety of tertiary amines having specific counter ions, it is more possible to modify structure in molecule of waterborne PUs obtained from cationomers. As a result of these modifications, additional hyrogen bonds and strong ionic effects are produced. These forces affect interactions of hardly miscible phases of hard segments consisting of urethane and urea groups with soft segments consisting of polyol groups, and alter surface free energy of the coatings obtained from PUDs prepared by using cationomers [66-67].

Non-ionic types of PUs are obtained by replacement of some part of hydrophobic polyol group with hydrophilic non-ionic building blocks, which are generally water soluble polyether polyols having ethylene oxide units in the structure. In order to prepare stable dispersions considerable amount of polyether segments must be incorporated in to the PU backbone. As a consequence of that, films obtained from nonionic dispersions results in water sensitive. These dispersions have an increasing number applications in wood, leather and plastic coating industries [66-67].

2.1.1 Methods for making waterborne polyurethane dispersions (PUDs)

Scientists have been developed various approaches for making PUDs in many years. Throughout decades of research, introduction of hydrophilic centers into a macromolecular chain of polyurethane polyurea molecule by using several processes is the basic principle to produce these dispersions. These hydrophilic centers consisting of ionic groups or ether groups are called as internal emulsifiers. Utilization of ionic groups can be made by reaction of certain diols in the prepolymerization stage or modified amines in the chain extension step of prepolymers. In this respect, several processes established for the synthesis of (PUDs) have been discussed by several researchers [65,68,69]. For all processes, first step is preparation of NCO-terminated polyurethane prepolymer through the reaction between diols (having ionic groups or nonionic groups) or polyols (macrodiols such as polyesters) and excess amount of isocyanates or polyisocyanates. Dispersion of the prepolymer and increase in the molecular weight are critically important steps that can be varied in several processes [70-73]. The four main process used for the preparation of waterborne PUDs: acetone process (solution process), prepolymer mixing process, hot-melt process and ketamin/ketazine process, are well explained below, respectively.

Acetone process (Solution Process): Acetone process, which can be easily perfomed and yielding fine dispersions, yet having disadvantage of obtaining low yield because of using large amount of solvent, have been well discussed and performed in many literatures [65,68,69,73-79,80-90]. In this process, hydrophilically modified NCO terminated prepolymer having high viscosity is dissolved in low boiling point solvent such as acetone in order to decrease the viscosity and complete subsequent chain extension reaction. As the water is introduced by slowly mixing in the solution, dispersion is obtained as a result of occurence of phase inversion yielding water as continuous phase in the system. Finally removal of solvent is done via distillation, yielding a solvent free aqueous PUD [65,68,69]. Scheme of preparation of aqueous polyurethane dispersions via acetone process is presented in Figure 2.1.

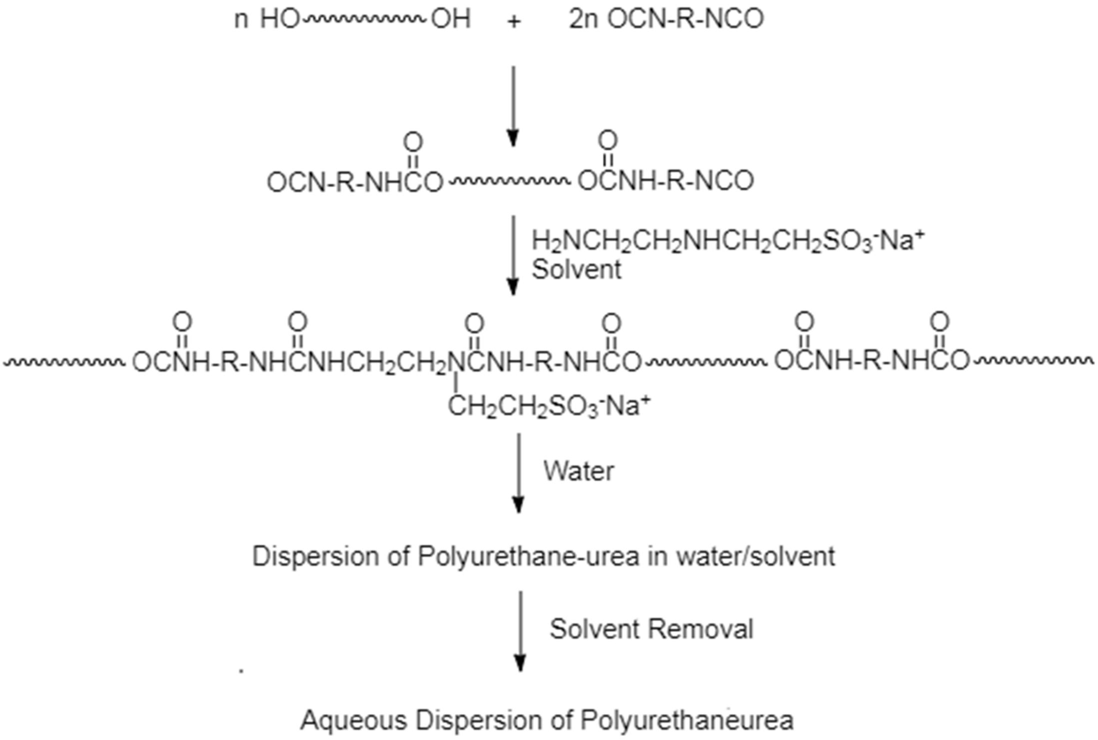

Figure 2.1 : Preparation of aqueous polyurethane dispersions via acetone process.

Prepolymer mixing process: Prepolymer mixing process based on two steps. In the first step NCO-terminated polyurethane prepolymer, is obtained in a water miscible organic solvent such as N-methyl pyrrolidinone (NMP) in order to reduce the viscosity of the medium. In this step the prepolymer is obtained from the reaction of excess molar amount of diisocyanates or polyisocyanates with diols having ionic groups (i.e. carboxylates or sulfoxylates) and polyols..

Then subsequent addition of water is followed to complete the dispersion under high speed agitation. The final chain extension step is done by using water soluble diamines or polyamines. Scheme of preparation of aqueous polyurethane dispersions via prepolymer mixing process is presented in Figure 2.2.

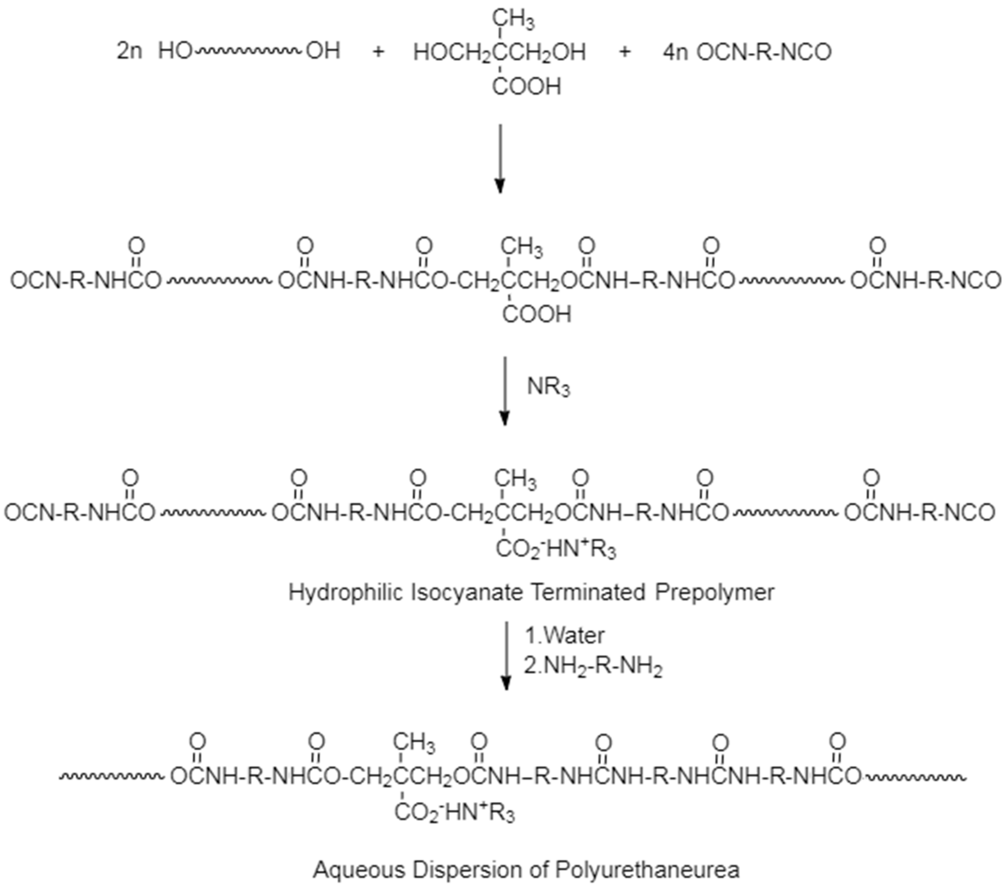

Figure 2.2 : Preparation aqueous polyurethane dispersions via prepolymer mixing process.

Hot melt process: In hot melt process, NCO-terminated ionically modified prepolymer prepared in melt is further reacted with excess urea at a temperature as high as 130 °C to form hydrophilic biuret oligomer. Without using any solvent, oligomer can be easily dispersed in water and chain extended by methylolation reaction of biuret groups with formaldehyde. However, requirement of special powerful agitators for highly viscous reaction medium, and hard control of formaldehyde reaction are the main disadvantages of this process. [65,89,101,102].

Ketimine/Ketazine process: Ketimines and ketazines are formed by the reaction of ketones with diamines and dihydrazines, respectively. In this process, ketimines and ketazines, which are used as chain extender can be mixed with NCO-terminated ionically modified prepolymer without any reaction. After addition of water, they can be hydrolyzed, resulting in diamines and hydrazines which can react NCO groups of prepolymers [65].

2.1.2 Chemistry and ingredients of polyurethane dispersions

It is known that a unique microphase separation structure occurs in PUs due to existence of alternating sequences of soft and hard segments in it structure, illustrated in Figure 2.3.

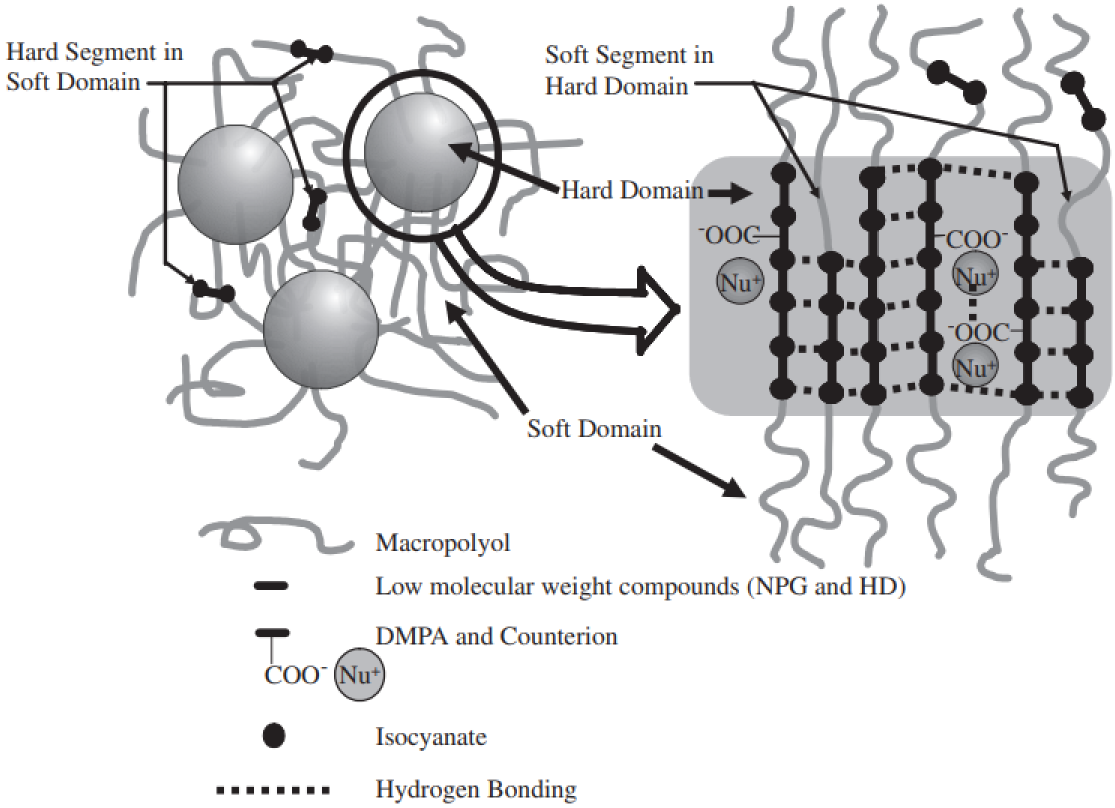

Figure 2.3 : Schematic illustration of microphase seperation structure of a film produced from PUD [154].

PU ionomers have obtained much more attention due to their possible incorporation into either hard or soft segments. Soft segments are flexible and have low polarity. Hard segments, consisting of urethane and urea groups, have polar structure and ability of interaction via hydrogen bonds. Besides their being prone to interacting with each other and aggregate, ionic groups are also linked to the so-called alien hydrophobic neighborhood. The chemical structure and compositional variation, the block length, and the ionic and urea content affect the final properties of PUDs. Microdomains are resulted from phase separation of two segment types due to inter-urethane/urea hydrogen bonding [102,103]. Hydrogen bonding in urethane/urea groups, columbic forces (electrostatic interaction) between ionic groups and crystallization of both hard and soft segments are pushing forces for formation of microdomains. The presence of microdomains provides good adhesion, cohesion and mechanical properties to polyurethane dispersions. Polarity difference, segment length, crystallization ability of each segment, intra and inter-segment interactions, over all composition of the PUDs are the major factors affecting this phase behavior [100,104-109]. Due to this segmented structure, there generally exist two Tg values consisting high Tg hard segment and low Tg soft segment. Interactions between the ionic groups and between hard and soft segments mostly determine the properties of polyurethane ionemers. Furthermore, viscosity of final dispersions are generally determined by particle size and volume portion of dispersed polymers, which is independent from molecular weight of polymer.

Major ingredients for preparation of waterborne PU and PU-ureas includes polyol, isocyanate, chain extender, internal emulsifier and catalyst, respectively.

Polyols are macromolecules containing hydroxyl groups and having medium-high molecular weight from 1000 to 8000 g mol^{-1}. Soft segment of PU and PU-ureas gives flexibility to the system, consists of polyols in the structure. There are many different types of polyols with respect to their molecular weights, functionalities and chemical natures, as well. Due to the this fact, different properties can be easily obtained by using different types of polyols. There are some exemplary studies published investigating effect of type of polyol on the properties of final products [110,111]. Thermoplastic and thermoset properties of final dispersion can be determined by the functionality of polyols in which macro diols with a functionality of 2 yield thermoplastic films whereas polyols with higher functionalities yield crosslinked thermoset systems. [112-114]. With respect to their chemical natures, there are commercially available three kinds, which are polyethers, polyesters and polycarbonates used in the preparation of PUDs. Generally polyesters show excellent resistance to light and ageing and higher strength and oil resistance with comparison to polyethers whereas polyethers provide improving water dispersion and more flexibility to the films. Polycarbonates generally presents good hydrolysis and oil resistance and greater mechanical properties [115-117].

Isocyanates are another major ingredient necessary for preparation of PUDs. Diisocyanates, consisting of aromatic and aliphatic structures, are the most commonly used for the synthesis of PUs, among many types of isocyanates [118]. Reactivity of diisocyanate are determined by its aromatic nature or aliphatic nature. Aromatic diisocyanates have much more reactive than aliphatic ones. Therefore, aromatic diisocyanates such as 2,4- or 2,6-toluene diisocyanate (TDI) or 4,4’- diphenyl methane diisocyanate (MDI) are mostly not preferred to be used in the synthesis of PUDs due to their higher reactivity with water and tendency to result in high viscosities causing difficulties to the dispersion process [119]. Therefore, HDI, IPDI and HMDI are mostly used in the synthesis of PUDs. Besides their lower reactivity, these types of diisocyanates also enhance the resistance to yellowing in films [119,120].

Chain extenders generally consist of difunctional, low molecular weight compounds which are further reacted with NCO groups of prepolymers [121,122]. However, chain extenders with higher functionalities can also be preffered if a crosslinked PUD structure is required. There are different types of diamines such as ethylene diamine, tetramethylene diamine, hexamethylene diamine, and polyamines such as diethylene triamine, adipic dihydrazide, which can be used as chain externders and diols such as butanediol, neopentylglycol. The use of diamines as chain extenders forms urea groups, resulting in systems with higher mechanical strength [118,123].

Internal emulsifiers can be differentiated as nonionic or ionic, where ionic groups can also be classified as cationic or anionic, depending on the functional group [70]. Poly(ethylene oxide) groups is major nonionic internal emulsifier used in the synthesis of nonionic PUDs. Due to its water sensitive behavior, nonionic types are not widespread yet they are well preferred for breathable coating applications [71,124]. With respect to ionic emulsifiers, anionic and cationic PUDs have different pendant ionic groups in polymer backbone, which can be an acid or tertiary nitrogen groups, be neutralized or quaternized, respectively in order to form their water soluble salts [125,126]. Between anionic emulsifiers, particularly 2,2-bis(hydroxymethyl) propionic acid (DMPA) and other compounds such as 2,2-bis(hydroxymethyl)butyric acid (DMBA) or sulfonated agents like diamino alkane sulfonates are commonly employed in the synthesis of anionic waterborne PU and PUD [63,127,128]. On the other hand, N-methyl diethanolamine is mostly preferred to be used as cationic emulsifier [127,129,130]. Both anionic and cationic PUDs are widely used in adhesives, textiles, coatings, automotive topcoats applications despite of the fact that anionic PUDs are commercially more dominant than cationics [131].

Catalysts are necessary to be used as an ingredient in the preparation of PUDs in order to force the reaction between hydroxyl and isocyanate groups even at low temperatures. Tertiary amines like 1,4-diazabicyclo octane, triethylamine or organo tin compounds, particularly dibutyltin dilaurate (DBTDL) and stannous octoate are used [126]. However less harmful catalysts like zirconium based compounds have been also advanced [119,132].

2.2 Polyacrylates

Polyacrylates are found to be increasingly used in many fields of applications as new methods for manufacturing of acrylic acids and acrylate esters are developed, which have actually been known since the middle of 19th century. As having carbonyl group neighboring vinyl group, acrylates can be simply polymerized by radical polymerization.

The basic members of polyunsaturated carboxylic acids are acrylate and methacrylate esters and their derivatives. N-butyl acrylate (BA), ethyl acrylate (EA), 2-ethyl hexyl acrylate (EHA), methyl acrylates are well known examples of acrylate esters which are commercially available. Methyl methacrylate (MMA), butyl methacrylate (BuMA), 2-ethyl hexyl methacrylate (EHMA) are well known examples of methacrylate esters, which are commercially available.

2.2.1 Polymerization techniques for polyacrylates

There are two techniques used for production of acrylic polymers, which are solution polymerization and emulsion polymerization, chosen with respect to desired properties and the planned application of the subsequent polymer.

Solution polymerization is a polymerization technique based on heating the monomer and initiator in the presence of a solvent which can be distilled or removed by spray-drying technique at the end of the process. Suitable solvents for the polymerization of acrylates of long-chain alcohols are aromatic hydrocarbons such as benzene and tolüene, whereas suitable solvents for the polymerization of acrylates of short-chain alcohols are esters and ketones. Selection of solvent with respect to its boiling point and chain transfer constant is very crucial since these properties of solvent can affect polymerization rate, viscosity and molecular weight of resulting polymer. Moreover, these factors are also known to be influencing mixing rate of reactor contents and removal of the heat of the polymerization [134]. Suitable initiators for this technique are soluble azo compounds, peroxides or hydroperoxides which can be used in concentrations of 0.01-2.00 wt % relative to the monomer. There are two methods which can be applied to solution polymerization process. First method is all in one or oneshot in which all monomers, solvent, initiator and other modifiers are charged together into reaction vessel at the beginning and heated to the polymerization temperature. Second method is the drip-feed or continuos process in which monomers and initiators are fed seperately into the solvent at polymerization temperature. Polymerization temperature, monomer concentration, type of solvent, concentration of initiator and choice of chain-transfer agents are major factors influencing solution polymerization [133].

Emulsion polymerization is a polymerization technique providing advantages for final product and process which is based on polymerization of oil soluble monomers in water in the presence of surfactant system, initiator, modifier and buffer [134]. Polymerization temperature and time, monomer concentration, initiator and choice of chain-transfer agents are major factors influencing final properties of polymers produced via emulsion polymerization. Due to their easily handling and non-hazardous properties compared to solution based ones, acrylic emulsion have very wide application areas such as coatings, sealants and adhesives, and as cement modifiers.

2.3 Preparation of Urethane/Acrylic Hybrid Dispersions

There are generally 3 main processes used for the preparation of the urethane/acrylic hybrid dispersions described as below, which have been reported and described in many patents and articles since 1970s [136-137].

Seeded emulsion polymerization technique is one of them. There are two approaches used in seeded emulsion polymerization technique. First one is the polymerization of acrylic monomers via free radical polymerization around the seed particles which are water dispersible and fully chain extended polyurethane particles. Second one is an enhanced process based on grafting. In this process, ionically modified PU prepolymer is further reacted with any type of hydroxyacrylate monomer to introduce vinyl groups to the prepolymer chain and then grafting is conducted between acrylic and polyurethane moeities. Since PU prepolymer has ionic groups on the backbone, polymerization of acrylic monomers might be carried out without usage of extra surfactant in the presence of PU seed, and urethane/acrylic hybrid dispersions are obtained with this process [136,138-149].

Miniemulsion polymerization is another method by which urethane/acrylic hybrid dispersions are prepared through the polymerization of acrylic monomers, in which the pre-formed urethane prepolymer and costabilizer such as hexadecane or hexadecanol or oil-modified polyurethane are dissolved in the miniemulsion droplets. These miniemulsion dropletes are created by miniemulsification of a mixture of surfactant solution and oil phase via high shear forces. Miniemulsion polymerization can be carried out using oil-soluble or water-soluble initiators [137,149,150].

Another method is *microemulsion polymerization* in which less polymer content and high surfactant content are required in order to achive nanosized latex particles. In a similar manner with above mentioned methods, acrylic monomers are polymerized via swelling in micelles or aggregates formed by water dispersible low molecular weight urethane prepolymer and polymeric surfactants in aqueous media [146,151,152].

2.4 Direct Coating on Textile Substrate

Coating on fabric is described as application of a polymer in the form of a thickened aqueous dispersion or aqueous or solvent solution via spreading on the fabric, resulting in a continuous layer. In order to prevent sinking of polymeric material into or through the fabrics, thickener should be used to thicken the polymeric dispersion or solution and thickened liquid should be well stirred and viscosity of it should be checked before application. Direct method is the basic and most popular coating procedure. There are two methods used for direct coating application, which are knife or blade on air and knife or blade over roller. For both ways, in order to make an even uniform surface on the fabric, fabric is well stretched flat and polymer as thickened form is applied under a stationary doctor blade. In knife or blade on air method illustrated in Figure 2.4, knife or blade attracts with fabric by touching its surface and scrapes the polymer resin on the surface of fabric as the fabric moves forward, which allows spreading of the polymeric resin or compound uniformly on the fabric.

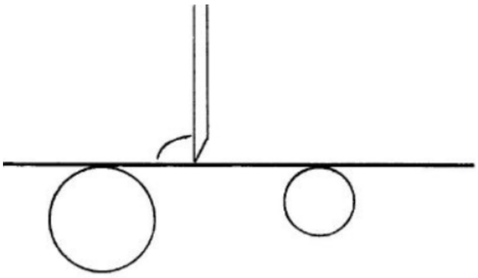

Figure 2.4 : Schematic illustration of knife or blade on air coating [153].

In the knife or blade over roller method,which is shown in Figure 2.5, there is a gap between knife or blade and fabric surface, allowing more thicker coating formation on surface of the fabric. For this method, amount of polymer coated should be adjusted with respect to solid content. In addition other parameters such as viscosity, fabric speed, construction, and etc. should also be checked since it can influence polymer add on.

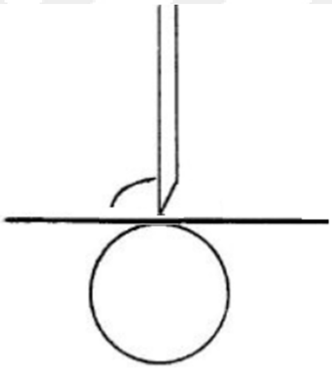

Figure 2.5 : Schematic illustration of knife or blade over roller method [153].

When the application of polymeric material onto fabric is completed, coated fabrics are dried off in the drying oven which is very crucial process. In order to prevent any defects appeared on coating drying should be processed gradually. The temperature of the first chamber of a multi chamber oven should be adjusted below the boiling point of the carrier liquid in order to provide a uniform drying of coating material. Then the temparature should be raised at remaining heating chamber. In order to crosslink the coating material yielding desired film formation the fabric should have well coated with resin. [153]. Figure 2.6 presents an exampliary schematic diagram of direct coating system [155].

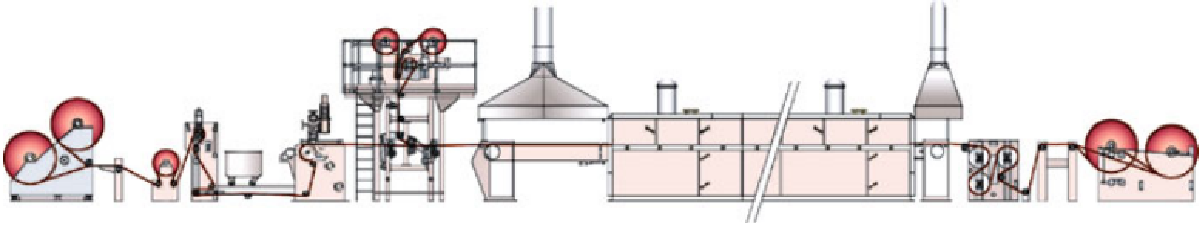

Figure 2.6 : Schematic illustration of a direct coating system [155].

2.5 Coloration of Textile Substrates with Pigments

Due to higher consumption of water in textile plants resulting in high load of waste water causing envoironmental pollution, pigment colouration system, by padding or printing, becomes more popular in which post wash treatment is no required [156-157]. Since pigments have little or no affinity to any fiber types, a film forming material, so called binders, are used to attach pigments to the fibers by capturing pigment particles in formed film matrix onto fibre [159,160]. Pigment binders are generally polymer latexes produced via emulsion polymerization of monomers such as acrylates, viny acetate, styrene, and etc. Choice of binder is very important since it directly influences the final properties such as coloring yield, dry and wet crocking fastnesses, wash fastness and touching feel of printed or dyed fabrics with pigment colors. Therefore, there are continuos works for advancing binder polymers by changing chemistry in order to obtain ideal binder for pigment coloration [161].

3. EXPERIMENTAL

3.1 Materials

Hexamethylene diisocyanate (HDI) was kindly gifted from Vencorex; 2-[(2-aminoethyl)amino]ethanesulfonic acid sodium salt (AAS salt) was kindly gifted from Evonik; polyester polyols (PES) (Mn~1000, 2000, and 3000 g mol^{-1}) were kindly gifted from Kururay. Acetone (high purity) was purchased from Tekkim; dibutyltin dilaurate (DBTDL, 95%), 2-hydroxy ethyl acrylate (HEA, 96%, contains 200-650 ppm monomethyl ether hydroquinone (MEHQ as inhibitor), butyl acrylate (BA, 99%, contains 10-60 ppm MEHQ as inhibitor), ethyl acrylate (EA, 99%, contains 10-20 ppm MEHQ as inhibitor), ammonium persulfate (APS), sodium thiosulphate ($Na_2S_2O_3$), sodium dodecyl sulfate (SDS) and dibutylamine (99.5%) were all purchased from Sigma-Aldrich. Toluene (≥99.9%), isopropyl alcohol (IPA, ≥99.8%), sodium hydroxide (NaOH, 0.1 N), hydrochloric acid (HCl, 0.1 N), bromophenol blue were purchased from Merck. DURAPRINT RED FDRL was kindy gifted from DURANER BOYA A.Ş.. RUCO-COAT TH 5020 was kindly gifted from RUDOLF CHEMIE. All materials were used as received.

3.2 Synthesis of Ac Emulsion

Pure Ac polymerization was done through a conventional emulsion polymerization process: a given amount of water was located in a reactor of 500 ml equipped with thermometer, stirrer and reflux condenser. Surfactant (SDS) and monomers were then added and stirred at 250 rpm using afore-used anchor type impeller. Ac monomers (BA, EA, HEA) were added and emulsified by agitating the mixture at 800 rpm for 15 min to make a pre-emulsion of acrylic. The reactor was then placed in a water bath pre-set at 75 ◦C with reduced stirring at 250 rpm; a solution of ammonium persulfate and $Na_2S_2O_3$ was added to start the polymerization, which lasted for 6 h.

3.3 Synthesis of PUDs

A series of PUD was synthesized in a 250-mL jacket glass reactor equipped with a mechanical stirrer, a nitrogen inlet, and a condenser. A circulating water bath was used to keep the reaction temperature constant. In a typical reaction, calculated amount of polyol (polyester polyol) and diisocyanate (HDI) were fed into the reactor together with 1000 ppm DBTDL catalyst. The reaction mixture was heated to 85ºC and mechanically stirred (300 rpm) under inert atmosphere for 4 h until the theoretical value of NCO groups was reached. The change of NCO value during the reaction was determined by dibutylamine back titration method. Then acetone is added in order to decrease viscosity and the calculated amount of AAS salt was added into the system to react with residual NCO groups and form chain-extended PUDs. After reaction is completed, calculated amount of water is added to obtain 30% (w/w) solids content after removal of acetone. A schematic illustration of the chemical route for synthesis of PUDs in scheme illustrated in figure 3.1 and the basic recepies of PUDs are shown in Table 3.1.

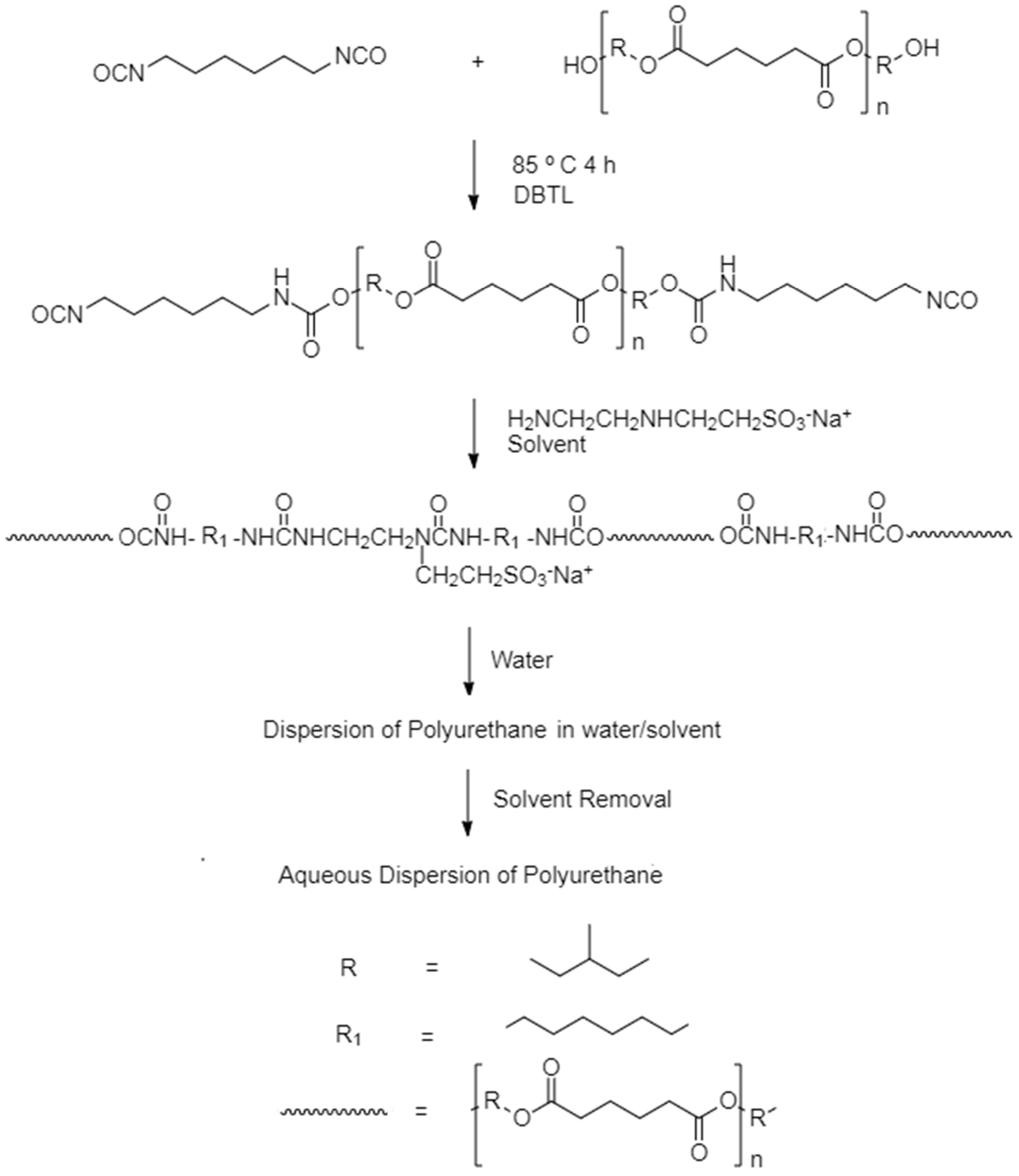

Figure 3.1 : Schematic illustration of the chemical route for synthesis of PUDs.

Table 3.1 : Basic recipes of PUDs.

PUD	M.W Polyol (g/mol)	NCO/OH	Chain Extender (% wt.)
R-1	1000	1.5	-
R-2	2000	1.5	-
R-3	3000	1.5	-
R-4	1000	2.0	-
R-5	2000	2.0	-
R-6	3000	2.0	1.0
R-7	3000	2.0	2.5
R-8	3000	2.0	5.0

3.4 Synthesis of PU/Ac Hybrid Dispersions

After the formation of the NCO terminated anionic PU prepolymer synthesis, calculated amount of HEA was added into the reaction mixture. The reaction was continued for 30 min and formation of vinyl terminated PU prepolymer was confirmed by FTIR. Copolymerization of vinyl terminated PU prepolymer with BA and EA was carried out through emulsion polymerization, a calculated amount of initiator solution (APS and $Na_2S_2O_3$) was introduced into the reactor under continuous stirring at 75 ^oC. Reaction was completed after 3 h and confirmed by FTIR. After removal of acetone, white milky emulsion was obtained. A schematic illustration of the chemical route for synthesis of PU/Ac hybrid dispersions is given in Figure 3.2 and basic recipes of PU/Ac hybrid disperisons are shown in Table 3.2.

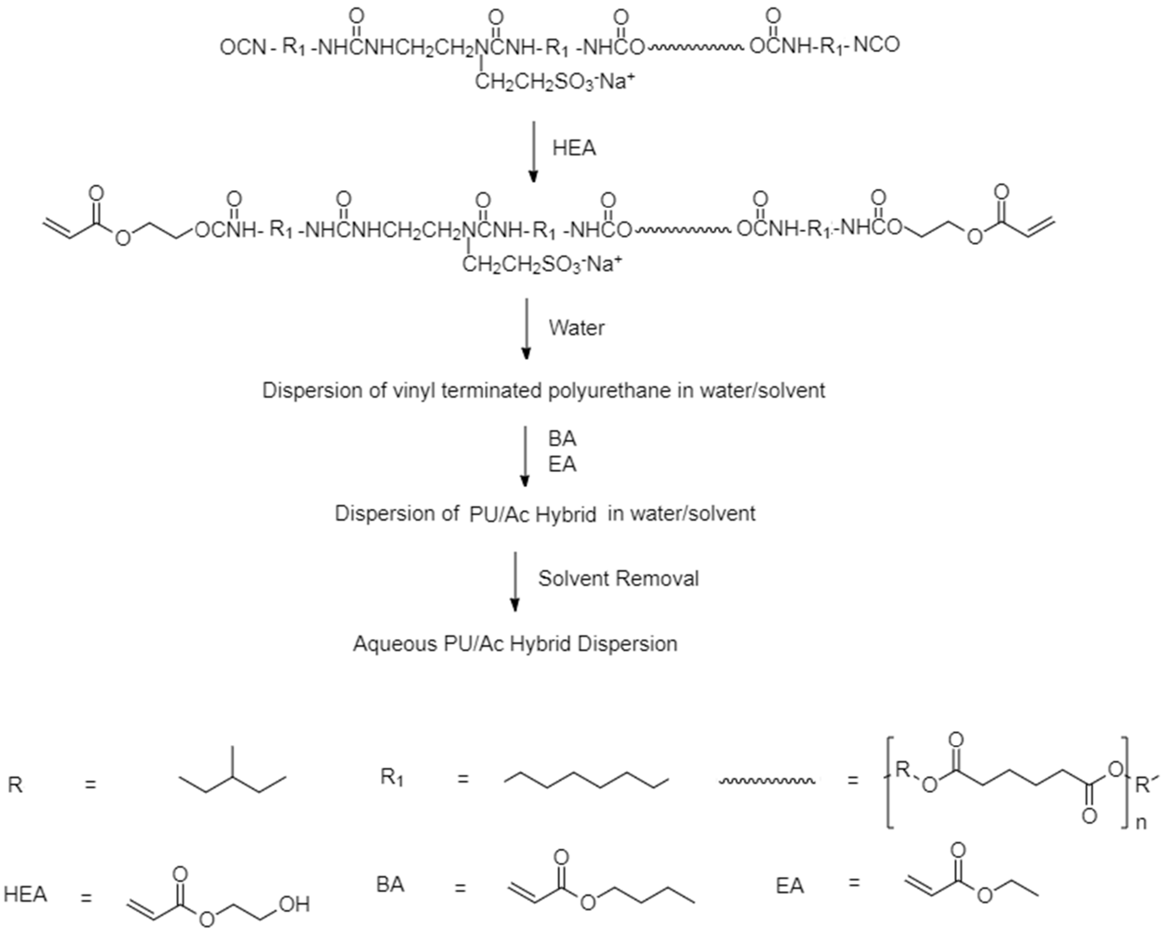

Figure 3.2 : Schematic illustration of the chemical route for synthesis of PU/Ac hybrid dispersions.

Table 3.2 : Basic recipes of PU/Ac hybrid dispersions.

Sample Code	M.W Polyol g/mol	NCO/OH	BA/EA (% wt.)
R-9	N/A*	N/A*	30
R-10	1000	2	5
R-11	1000	2	10

*N/A : Not applicable

3.5 Preparation of Films

In order to prepare films from Ac emulsion, PUD and PU/Ac dispersions, about 30 g of dispersion was placed in a silicon mold and allowed a slow evaporation of the water at room temperature for 48 h. Afterwards, the casting film was dried for further 48 h at 70 ^{o}C h to allow the complete removal of water.

3.6 Coating on Fabrics

Black woven 100% cotton fabric was chosen in order to see the differences of appearances of coated dispersions and white woven 100% cotton fabric was chosen for pigment paste coating. Duraprint red FDRL was used as red pigment. All dispersions were directly pasted with Ruco-coat TH 5020 as having same viscosity around 5000 mPas and applied on the fabrics using lab scale blade on air coating. After coating, they were firstly dried at 130 °C for 1 minutes and then fixed at 170 °C for 2 mins.

3.7 Characterization

3.7.1 Chemical characterization

Chemical structure of Ac emulsion, polyurethane dispersions, vinyl terminated polyurethane and acrylate grafted polyurethane were confirmed by FTIR using IR-Prestige-21Shimadzu at R&D Center Laboratories of RUDOLF-DURANER.

3.7.2 Determination of residual NCO

Residual NCO in PU prepolymer was determined via classical dibutylamine method described in ASTM D2572-97 [162] .According to this method, 0.1 g of sample containing approximately 1.1 milliequivalents of free isocyanate was dissolved in 25 mL of dry toluene, and then 25 ml of 0.1N di-n-butylamine solutions was added and continued swirling for 15 min with stopper in place. 100 mL of IPA and 4 to 6 drops of bromphenol blue indicator solution were added and the solution was titrated with 0.1 N HCl to a yellow end point. The free isocyanate content was calculated by using the given Equation 3.1 below:

$$\text{Free Isocyanate \%} = \frac{\left[(B - V) \, x \, N \, x \, 0.042\right]}{W} x100 \tag{3.1}$$

where; B = volume of HCl for titration of blank (mL); V = volume of HCl for titration of the specimen (mL); N = normality of HCl (N); 0.0420 = milliequivalent weight of the NCO group; W = specimen weight (g).

3.7.3 Characterization of Ac emulsion, PUD and Ac/PU hybrid dispersions

Total solid contents were determined by using AccuDRY drying system. The solid content of the Ac emulsion, PUD and PU/Ac dispersions were determined by difference in weight before and after water evaporation. With this aim, about 1.0 g emulsion/dispersion sample was placed on an aluminium container and the water was evaporated at 105 °C in an oven until constant weight was reached The pH's were measured without any sample preparation using WTW inolab® pH 7110 table tab pH meter. The pH electrode was calibrated using the standard buffer solutions (4.01, 7.00 and 10.01).

The mean particle size and the particle size distribution of the Ac emulsion, PUDs and PU/Ac dispersions were measured in Mastersizer 2000 (Malvern) provided with laser diffraction and polarized light detectors. With this aim, a small amount of emulsion/dispersion sample was added to a deionised water tank and measurements were completed. The viscosities of the Ac emulsion, PUDs and PU/Ac dispersions were measured with Brookfield DV-E viscometer at 25 °C by using the spindle no. 4 @ 50 rpm. The phase stability of the acrylate emulsion and dispersions was evaluated by measuring the Delta backscattering (ΔBS) of monochromatic light (l¼ 880 nm) from the suspension employing an optical analyzer, Turbiscan Lab Expert (Formulaction, France). Ac emulsion, PUDs and PU/Ac dispersions in flat bottomed cylindrical glass tubes (70 mm height, 27.5 mm external diameter) were placed in the instrument, and the backscattering of light from dispersions was then periodically measured along the height at 40 °C for 24 h.

All of analyses mentioned above were performed at R&D Center Laboratories of RUDOLF-DURANER.

3.7.4 Characterization of films

Glass transition temperatures (Tg) were determined by using DSC 8000 (Perkin Elmer) differential scanning calorimeter at R&D Center Laboratories of RUDOLF-DURANER. The weak Tg's of acrylate emulsion, PUDs and PU/Ac dispersions were detected according to the method described by Perkin Elmer. The heat flow was measured under a heat rate of 20 °C min^{-1} in a range from –70 °C to 250 °C, quenching at –70 °C and re-heating under a heat rate of 20 °C min^{-1} in a range from –70 °C to 250 °C.

The tensile strength and elongation at break of the acrylate, PU and PU/Ac films were determined with Testform/AS1 (1 kN) Mechanical Testing Machine using dumb-bell test bars. Tensile testing was performed at Central Research Laboratory of Bursa Technical University according to the international standard ISO 37 [163] at room temperature with a crosshead speed of 500 mm/min. The Shore A hardness of the films was measured at room temperature by Mitech MH 14.05 Digital Shoremeter A according to BS ISO 7619-1 [164]. Results are the average values of five measurements. Shore A tests were performed at R&D Center Laboratories of RUDOLF-DURANER.

3.7.5 Characterization of coated fabrics

Black coated fabrics were evaluated visually and by hand-touching with respect to their glossiness and softness property. Color yield of the white fabrics coated by red color pigment were evaluated with Data Color 600 instrument using CIE Lab program. Their wet and dry rubbing fastness properties were determined by using James Heal's Crock Master with respect to ISO 105-X12:2016 [165].

All fabrics were washed with respect to BS EN ISO 6330: 2012 [166].Washed fabrics were compared with original coated fabrics and their washing resistance property were examined visually with respect to their glossiness, softness and pigment binding property. All the test methods were performed at R&D center laboratories of RUDOLF-DURANER.

4. RESULTS AND DISCUSSION

4.1 Properties of Ac, PU, PU/Ac Hybrid Dispersions

Properties of synthesized emulsion and dispersions were discussed in three parts subtitled as physicochemical properties, particle size and distribution and stability.

4.1.1 Physicochemical properties

FTIR spectras of PUDs together with HDI and PES (Figure 4.1a) , PU/Ac hybrid dispersions together with vinyl terminated prepolymer and prepolymer before HEA addition and Ac emulsion together with BA, EA and HEA (Figure 4.1b) are shown in Figure 4.1.

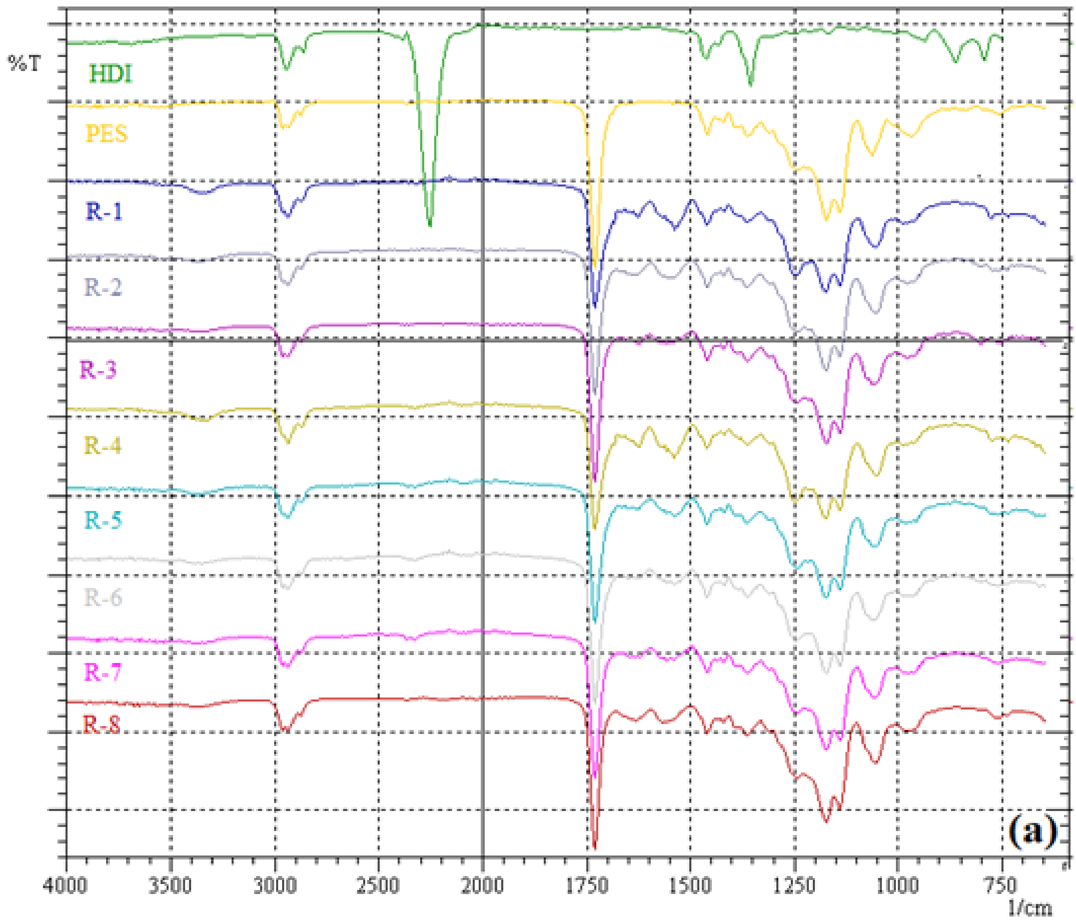

Figure 4.1a: FTIR spectra of HDI, PES and PUDs.

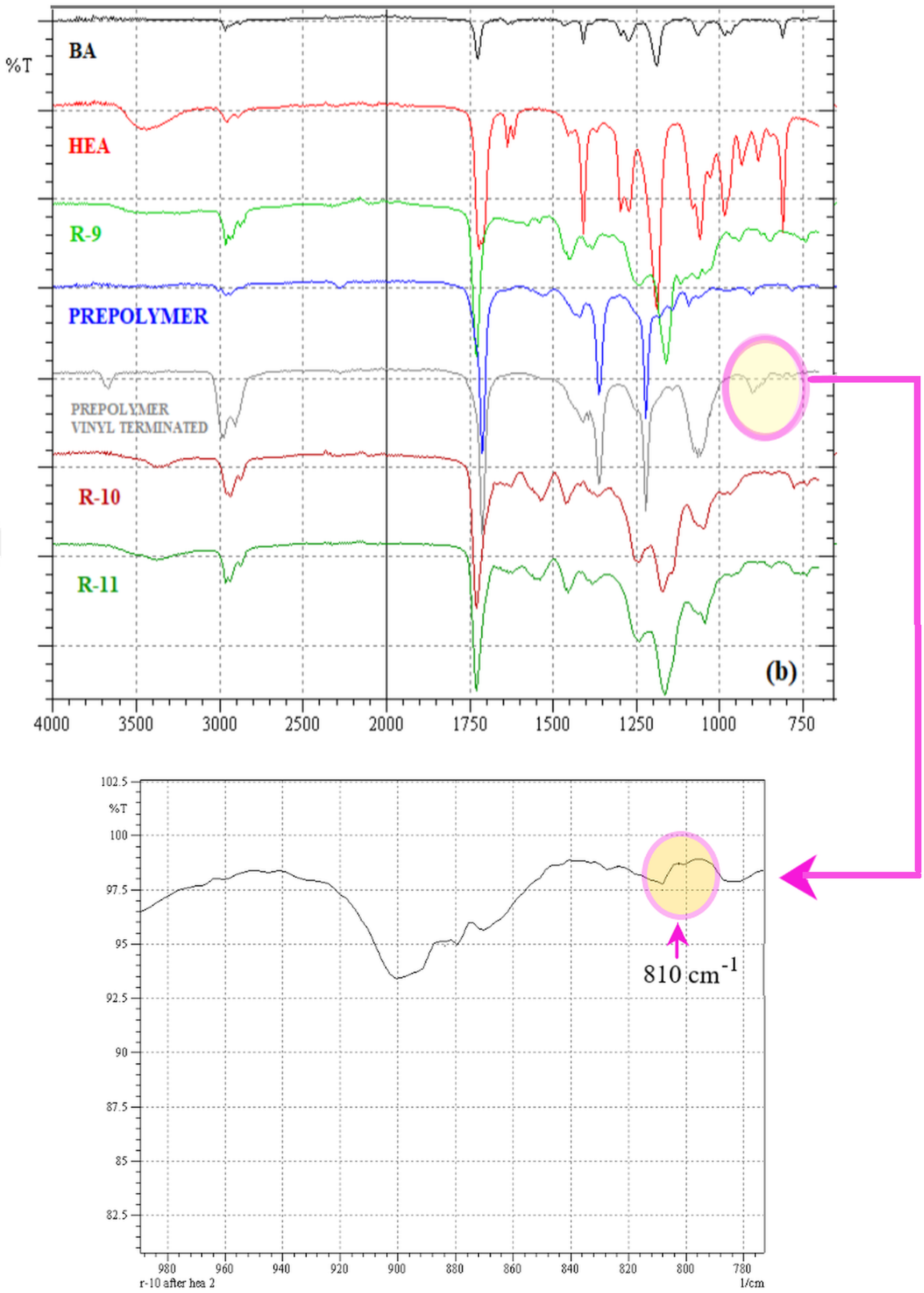

Figure 4.1b: FTIR spectra of BA, HEA, prepolymer, vinyl terminated prepolymer, Ac (R-9) , PU/Ac hybrid dispersions (R-10, R-11).

From Figure 4.1a, it was observed that there were only some differences in the relative intensities and positions of several bands were distinguished at the FTIR spectras of PUD samples. In general, the denser stretching peak arised at 2252 cm^{-1} is the characteristic -NCO peak of diisocyanate. For PUD samples, the dissapearance of this peak indicated the completion of the the reaction. In addition, the streching band arised at 3365 cm^{-1} was corresponded to the N–H streching, while the peaks arised at 1730 cm^{-1} and 1622 cm^{-1} were corresponded to the C=O streching peaks of urethane and amide, and the band at around 1537 cm^{-1} was corresponded to the NH stretching of urea. On the other hand, the spectras showed the characteristic C-O-C stretching, N-CO-O non-symmetric stretching (1240–1242 cm^{-1}; 1049–1060 cm^{-1}), and C-O-C stretching (1139 cm^{-1}; 948–962 cm^{-1}) bands of the polyol. Furthermore, it was concluded from the comparison of R-1, R-2 , R-3 and R-4, R-5, R-6 in theirselves that the intensity of the peaks arised at 3363 cm^{-1}, 1622 cm^{-1} and 1537 cm^{-1} decreased as the ratio of hard segment decreased and molecular weight of the polyol increased. From the comparison of R-6, R-7, R-8 in theirselves, the intensity of the peaks arised at 3363 cm^{-1}, 1622 cm^{-1} and 1537 cm^{-1} increased as the amount of ionic chain extender increased which was contributed in hard segment domain [167-168].

BA, HEA, prepolymer, vinyl terminated prepolymer, R-9, R-10, R-11 were all studied with FTIR shown in Figure 4.1b. It should be noted that spectra of EA was not shown due to less intense peaks on spectra because of its high volatility; however it exhibited similar spectra with BA. Characteristic peaks of acrylate monomers were arised at 2959 cm^{-1} corresponding to asymmetric CH_2 stretching; 2850 cm^{-1} corresponding to symmetric CH_2 stretching; 1730 cm^{-1} corresponding to C=O stretching; 1186 cm^{-1} corresponding to C–O, C–C stretching; 1640 cm^{-1} and 810 cm^{-1} corresponding to the C=C bond. The spectrum of R-9 revealed that polymerization reaction was completed due to the absence of peaks at 810 cm^{-1} and 1640 cm^{-1} corresponding to the C=C bond. Vinyl terminated PU prepolymer spectrum showed that characteristic -NCO peak of diisocyanate at 2252 cm^{-1} dissappeared as an indicator of completion of the reaction between NCO groups and HEA. Furthermore, addition of vinyl groups on to PU backbone was also confirmed with slightly appearance of the peak at 810 cm^{-1}. R-10 and R-11 were obtained from chain extension of vinyl terminated prepolymer with BA and EA. It was observed from Figure 4.1b that some peaks showed a significant change with the increasing acrylic content in the samples R-10 (5% Ac) and R-11 (10% Ac): The intensity of the peaks arised at 1622 cm^{-1} and 1537 cm^{-1} decreased as the acrylic content increased. It was also observed that with the increase of acrylic content, peaks arised at 1050 cm^{-1} were slightly splitted into two at 1060 cm^{-1} and 1040 cm^{-1} corresponding to N-CO-O non-symmetric stretching. Furthermore, the stretching band arised at 3365 cm^{-1} corresponding to the hydrogen-bonded N–H in both urethane and urea was broadened as the acrylic content increased. The decrement and broadening of the peaks might be attributed to good phase mixing and interaction of Ac and PU moeities in the materials [169].

Since physical properties of PUDs, Ac and PU/Ac hybrid dispersions such as solid content, pH and viscosity are important in terms of application, these properties were measured and reported in Table 4.1. All synthesized materials exhibited 27.5- 30.5 % wt of solid content in coherence with theoretical calculations. Furthermore pH of all emulsion and dispersions were found to be changed between 7.0-8.5 as expected. The viscosities of PUDs (R-1, R-2, R-3, R-4, R-5, R-6) were measured between 20 and 312 mPa. However, the variation of viscosity could not be attributed to any parameter such as NCO/OH ratio of PUDs or molecular weight of polyols. Yet, increase of chain extender amount, samples obtained from using same polyol at constant NCO/OH ratio (R6, R7, and R8) showed a bit increment in viscosity as it was expected. The viscosities of Ac (R-9), Ac/PU hybrid dispersions (R-10, R-11) were measured as 30, 15, 20 mPa, respectively. From comparison of viscosity of R-4 with viscosities of R-10 and R-11, it can be concluded that grafting with acrylate monomers resulted in decrement of viscosities of final dispersions. Furthermore, increment of acrylate content lead to slightly increment of viscosity.

Table 4.1 : Solid content, pH and viscosity values of PUDs, Ac and PU/Ac hybrid dispersions.

Sample Code	**Physical Properties**		
	Solid content (%wt.)	**pH**	**Viscosity (mPa.s)**
R-1	30.1	7.1	312
R-2	28.8	7.0	188
R-3	28.5	7.2	20
R-4	29.1	7.2	68
R-5	30.3	7.2	116
R-6	29.8	7.2	28
R-7	30.1	7.5	30
R-8	28.4	8.2	56
R-9	29.7	7.3	30
R10	27.6	8.5	15
R-11	27.5	8.3	20

4.1.2 Particle size distribution

The particle size distribution datas of PUDs, Ac and PU/Ac hybrid dispersions are presented in Figure 4.2 and Table 4.2. According to these data, particle size distribution of the PUDs were found to be variated due to the NCO/OH ratio, molecular weight of polyols and as well as the amount of chain extender and acrylate content. It could be concluded from the comparison of R-1, R-2 and R-3 in theirselves and R-4, R-5, R-6 in theirselves (Figure 4.2a) that PUDs became more uniformly distributed with the increase of molecular weight of polyol. Furthermore, from the comparison of samples prepared by using polyols with same molecular weights and different NCO/OH ratios (R-1 with R-4, R-2 with R-5, R-3 with R-6), more uniform distributions were observed with the decrease of NCO/OH ratio. Additionally it could be also seen from Figure 4.2b that with the increase of chain extender amount, samples obtained from using same polyol at constant NCO/OH ratio (R6, R7, and R8) showed more uniformly distributed and has a lower particle size range. From list of f 4.2c, it could be seen that Ac emulsion (R-9) gave a broad particle size distribution and for Ac/PU hybrid dispersions (R-10 with 5% Ac and R-11 with 10% Ac), increase in acrylate content had lead to more uniform distribution. From comparison of R-4 with R-10 and R-11, it could also be concluded that grafting with acrylate monomers resulted in more uniform distribution. The span shows the particle size distribution; the distribution of the particles became more uniform with the narrower span. According to the span data given in Table 4.2, all PUD samples were polydisperse and follows the order R-4>R-1>R-10>R-3>R-2>R-5>R-7>R-6>R-11>R-8.

It was determined from Table 4.2 that particle sizes of PUDs were changed between 0.2 and 35 μm. In addition, a significant decrease was observed as molecular weight was increased, for the samples R-4, R-5, and R-6, which were synthsized by using polyols having molecular weight of 1000, 2000 and 3000 g/mol, respectively at a NCO/OH ratio of 2.0. Additionally it could be also seen from Table 4.2 that R-8 had the lowest particle size due to the higher amount of sulfonate groups incorporated into PU polymer backbone via chain extension step. Particle sizes of R-9, R-10 and R-11 were found to be 88.70, 28.40, 31.55, respectively. From comparison of R-4 with R-10 and R-11, it could be concluded that particle size of the resulting dispersions were increased as the acrylate content increased. This polydisperse distribution and larger particle sizes could be affected from dispersion and emulsification processes after removal of acetone, chain extention process and mixing rate.

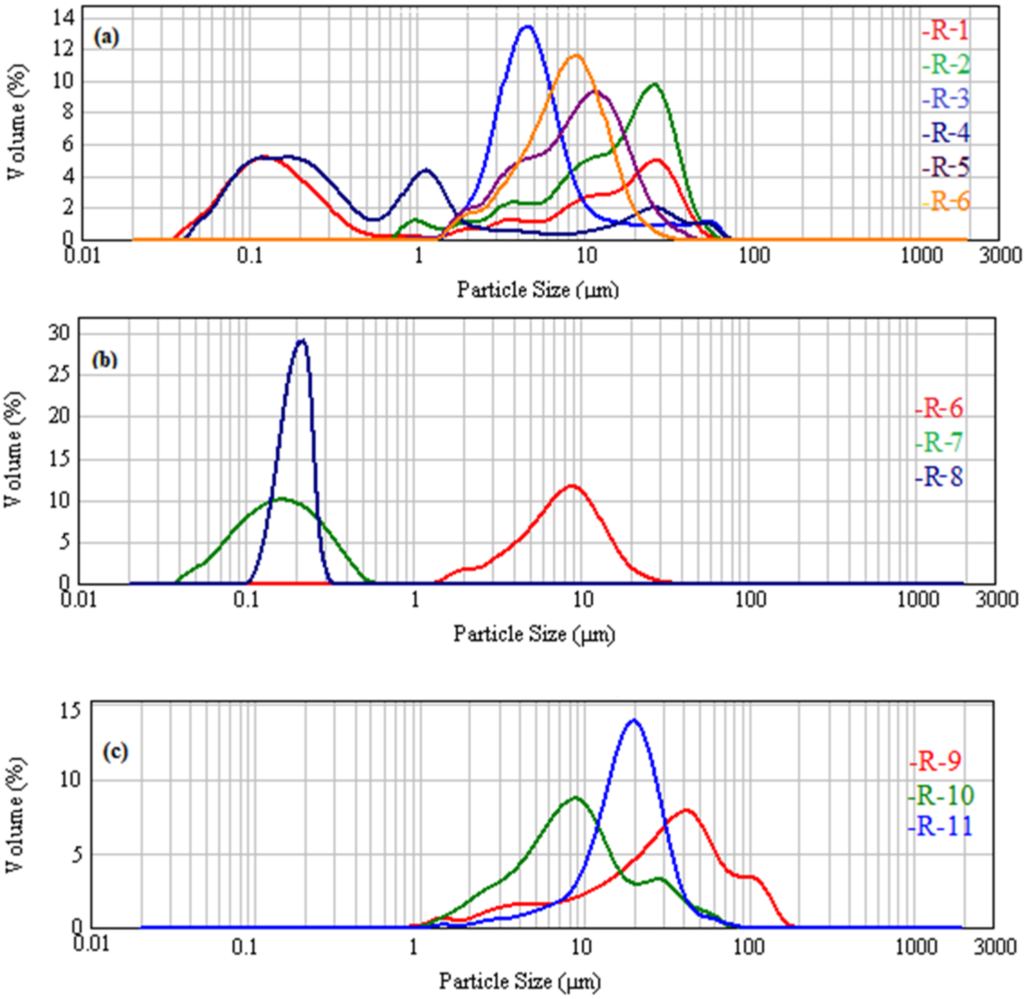

Figure 4.2: Particle size distribution of **(a)** PUDs, **(b)** PUDs with different chain extender amount, **(c)** Ac and PU/Ac hybrid dispersions.

Table 4.2 : Particle size distribution of samples.

Sample Code	**Particle Size Distribution (µm)**			
	d(0.1)[a]	**d(0.5)**[b]	**d(0.9)**[c]	**Span**[d]
R-1	0.082	1.334	29.896	22.351
R-2	3.273	16.949	34.702	1.854
R-3	2.785	4.872	13.445	2.188
R-4	0.087	0.310	21.567	69.189
R-5	3.112	9.241	19.493	1.773
R-6	3.409	7.969	14.754	1.424
R-7	0.083	0.204	0.385	1.476
R-8	0.149	0.200	0.249	0.500
R-9	5.208	32.058	88.70	2.604
R-10	2.956	8.533	28.399	2.982
R-11	8.659	18.551	31.547	1.234

[a] d(0.1): size of the particle below which 10% of the sample lies

[b] d(0.5): size of the particle below which 50% of the sample lies

[c] d(0.9): size of the particle below which 90% of the sample lies

[d] particle size distribution or $\text{"span"} = [d(0.9) - d(0.1)] \;/\; d(0.5)$

4.1.3 Stability

In this study, the stability of the PUDs, Ac and PU/Ac hybrid dispersions was investigated for 1 day at 40 ºC by means of the Turbiscan LAB. Turbiscan LAB, which is a non-destructive method (no sample dilution), is an effective tool for quick and global determination of the stability of emulsions and suspensions by giving Turbiscan specific parameter "TSI" which helps scientists to identify the destabilization mechanisms including particle migration (creaming and sedimentation) and particle aggregation (coalescence and flocculation). During given time interval, backscattering (BS) and/or transmission signal intensities will show variations with respect to destabilization phenomenon occuring in the sample. The higher the intensity varies, the less stable the sample is. The TSI calculation is given in equation 4.1 [170].

$$\mathrm{TSI} = \frac{\sum_h \left|\mathrm{scan}_{\mathrm{i}}(h) - \mathrm{scan}_{\mathrm{i\text{-}1}}(h)\right|}{H} \qquad \textbf{(4.1)}$$

Where h is (BS) and/or transmission light at all measured positions based on scan to scan difference and *H* is total height of the sample. From the calculation of TSI value, device software also creates destabilisation kinetics graphs showing TSI evolution during given time interval, which helps formulators to make more easily decision of more stable product. Figure 4.3 shows typical ΔBS data profiles for creaming, sedimentation (Figure 4.3a) and colalescence/flocculation (Figure 4.3b) behavior and example of destabilization kinetics graph including the explanation of stability (Figure 4.3c) [170,171].

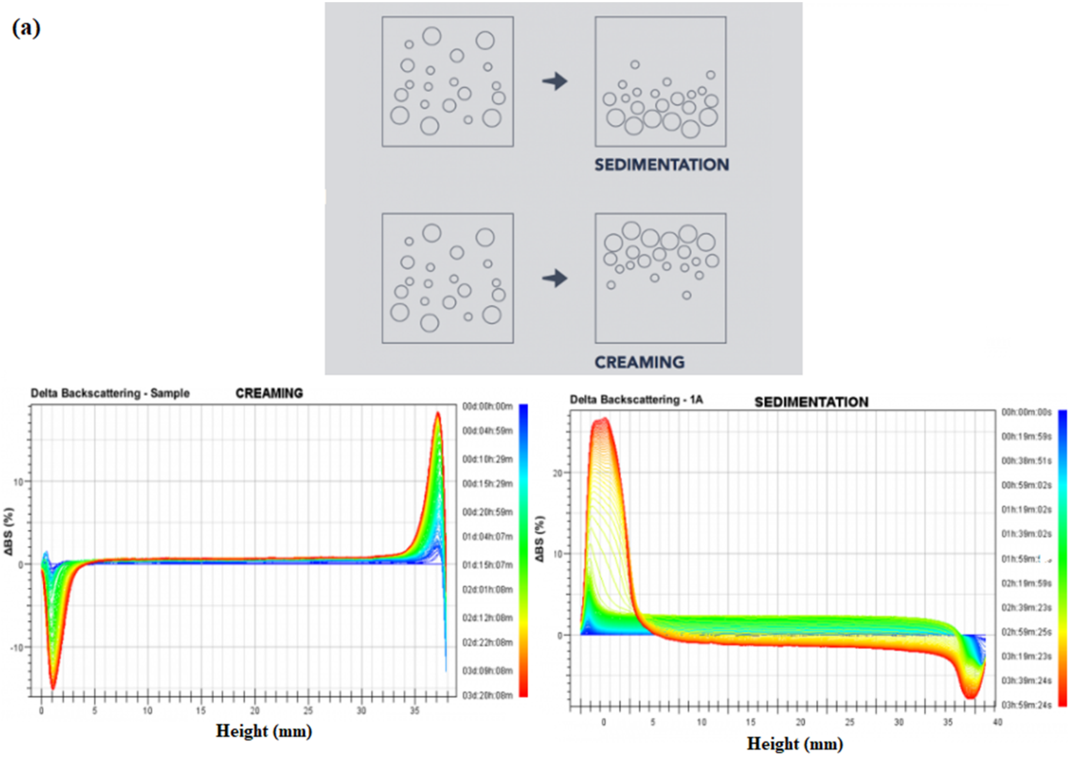

Figure 4.3a : Typical ΔBS data profiles for creaming and sedimentation [170,171].

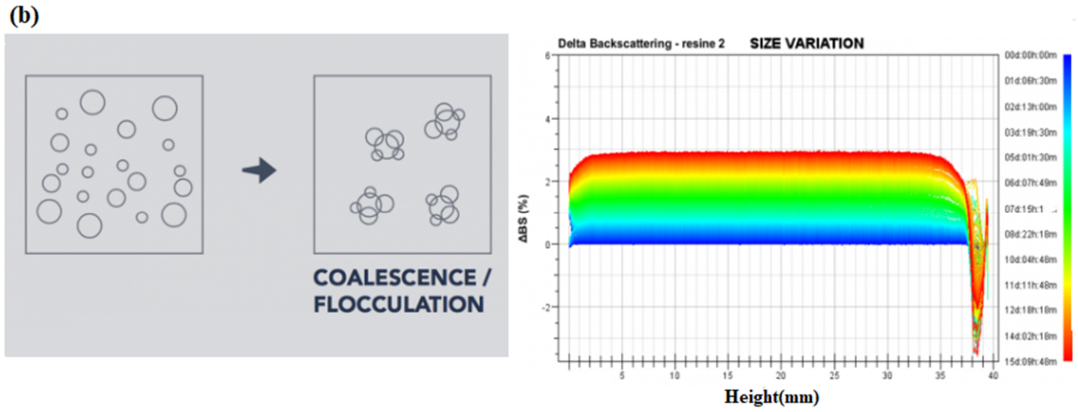

Figure 4.3b : Typical ΔBS data profiles for coalescence/flocculation [170,171].

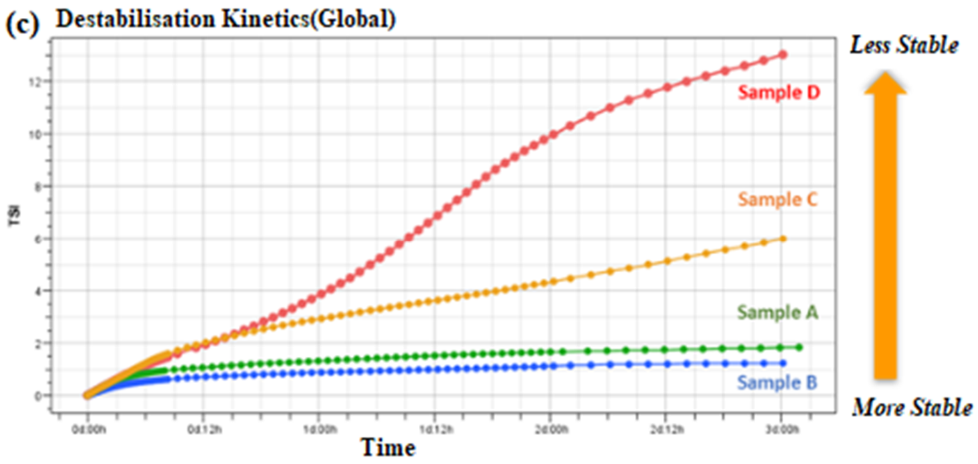

Figure 4.3c : Example of destabilization kinetics graph [170,171].

For the evaluation of stability of resulting dispersions, all the samples were well studied using Turbiscan LAB. The original ΔBS data profiles were all obtained from the software and presented in Figure 4.4. In positive or negative variations of the backscattering profiles of the different formulations were not correlated to destabilization processes under the sample height of 1 mm and over that of 40 mm, the values determined by enclosed air in the bottom and/or on the top of the cylindrical glass tube, respectively. Figure 4.4 shows ΔBS profiles of samples R-1, R-2, R-3, R-4 (Figure 4.4a), R-5, R-6, R-7, R-8 (Figure 4.4b), R-9, R-10 and R-11 (Figure 4.4c). The ΔBS of R-1 sample is close to the base line value during the entire time of analysis. This result evidenced that R-1 dispersion was stable and no destabilization process was observed during analysis. On the other hand, the backscattering profile of R-2 and R-4, R-5, and R-7 did not intersect the zero baseline and showed continuous negative peaks during the scan. However, for R-2 and R-5 the delta backscattering signals decreased as the destabilization progressed. From the analyze of delta backscattering signals at 24 h (red curve), we found that destabilization process was initiated by coalescence and it was dominated in the dispersion. R-1, R-4 and R-7 samples, were found to provide their stability during the analyze due to the constant delta backscattering signals at the top and the bottom of the samples.

For the sample R-3 a continuous variation of backscattering profile was observed with positive and negative peaks. Turbiscan profiles did not intersect the zero bases; a positive transmission profile is coupled with a negative backscattering one at the bottom of the sample. These findings are due to a time-dependent sedimentation phenomenon. In the initial period, coalescence was dominated in the PUD sample, which was evidenced by a progressive decrease in backscattering. As the coalescing droplets became bigger, they migrated from the top to the bottom of the sample. After 24 h, a decrease in bacscattering was observed at the bottom which showed sedimentation dominated in the PUD sample. On the other hand, a continuous variation of backscattering profile with positive and negative peaks was also observed for sample R-6 for the entire height of the sample. A positive transmission profile at the top of the samples is coupled with a negative backscattering one at the bottom. These findings are due to a time-dependent sedimentation phenomenon. Sample R-8 showed a continous increment of backscattering for the entire height of vial, which was possibly reasoned from the formation of aggregates via coalescence or flocculation.

As it can be seen in Figure 4.4c, R-9 and R-10 showed a sedimentation phenomena due to the increment of particles at the bottom, proved by positive increment of ΔBS (red curve) as the destabilization was progressed. However, there was a continous positive variation of ΔBS during rest height of whole vial observed for R-9, which was due to formation of aggregates, and a contious slightly positive variation of ΔBS in the middle of vial and negative variation of ΔBS observed for R-10, which was due to sedimention phenomena occurred at the bottom and clarification phenomena occurred at the top. The sedimentation phenomena was dominantly experienced for sample R-11. An intense increment of particles at the bottom of vial was led to continous positive variation of ΔBS, which was characteristic of sedimentation phenomena and there observed a continous negative variation of ΔBS at the top due to the clarification associated with sedimentation behaviour [172].

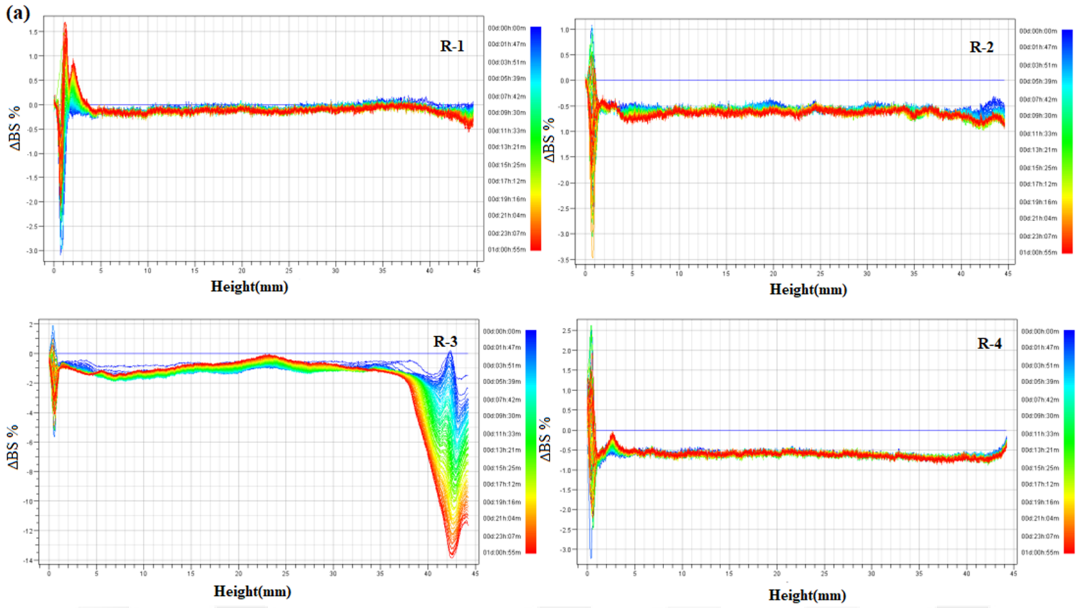

Figure 4.4a: ΔBS data for R-1, R-2, R-3, R-4.

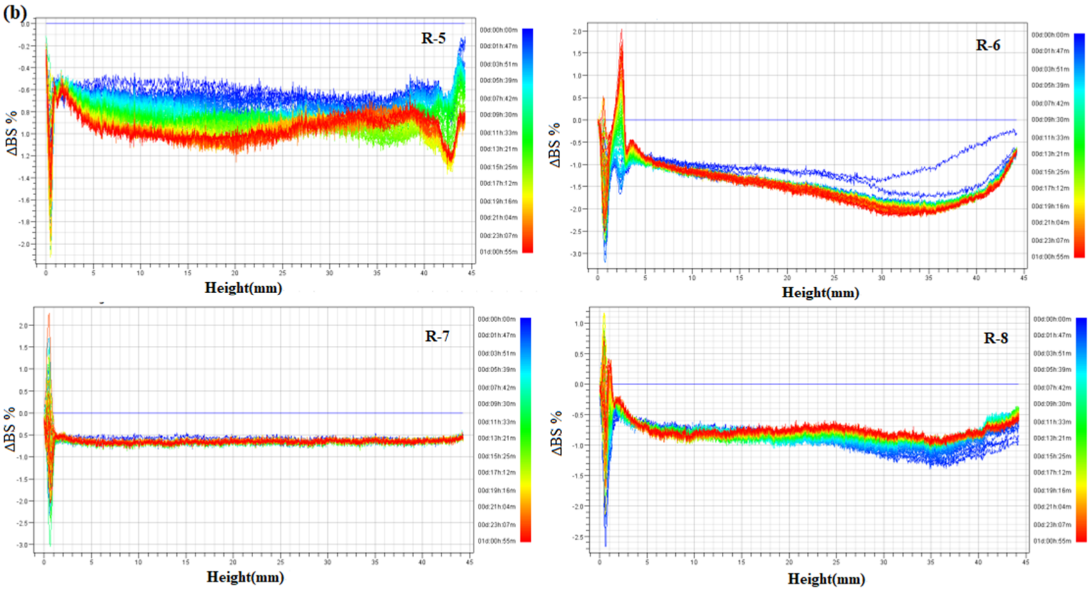

Figure 4.4b: ΔBS data for R-5, R-6, R-7, R-8.

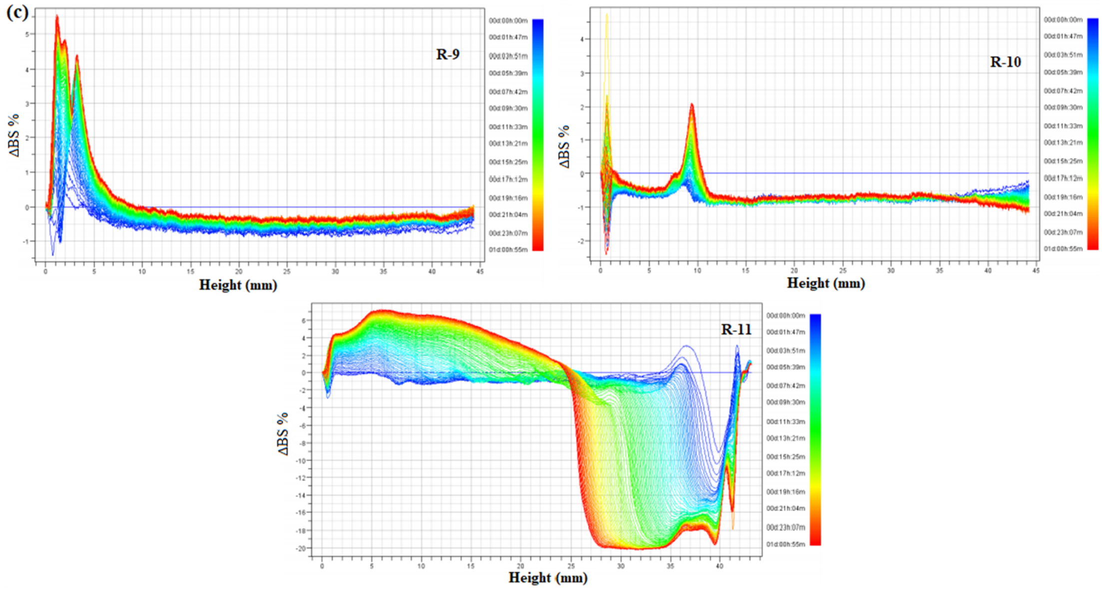

Figure 4.4c: ΔBS data for R-9, R-10 and R-11.

Destabilisation kinetics graphs are showed in Figure 4.5 while TSI values of samples at the end of 24 h are presenred in Table 4.3. According to Figure 4.5 and and Table 4.3, stability of the PUDs were found to be variated due to the NCO/OH ratio, molecular weight of polyols and as well as the amount of chain extender and acrylate content. It could be concluded from the comparison of R-1, R-2 and R-3 in theirselves and R-4, R-5, R-6 in theirselves (Figure 4.5a) that PUDs became less stable with the increase of molecular weight of polyol. Furthermore, it was observed from the comparison of the samples prepared by using polyols with same molecular weights and different NCO/OH ratios, that more stable dispersions obtained due to the decrease of NCO/OH ratio (comparison of R-1 with R-4, R-2 with R-5, and R-3 with R-6). Yet, for R-3 and R-6 the vice versa was found. Additionally it could be also seen from Figure 4.5b that for the samples R-6, R-7 and R-8, stability was increased with the increase of chain extender amount using the same type of polyol at constant NCO/OH ratio. From Figure 4.5c, it could be seen that Ac emulsion (R-9) was less stable than R-4. From comparison of R-4 with R-10 and R-11, it could also be concluded that grafting with acrylate monomers resulted in less stable product and increase in acrylate content resulted in less stable product.

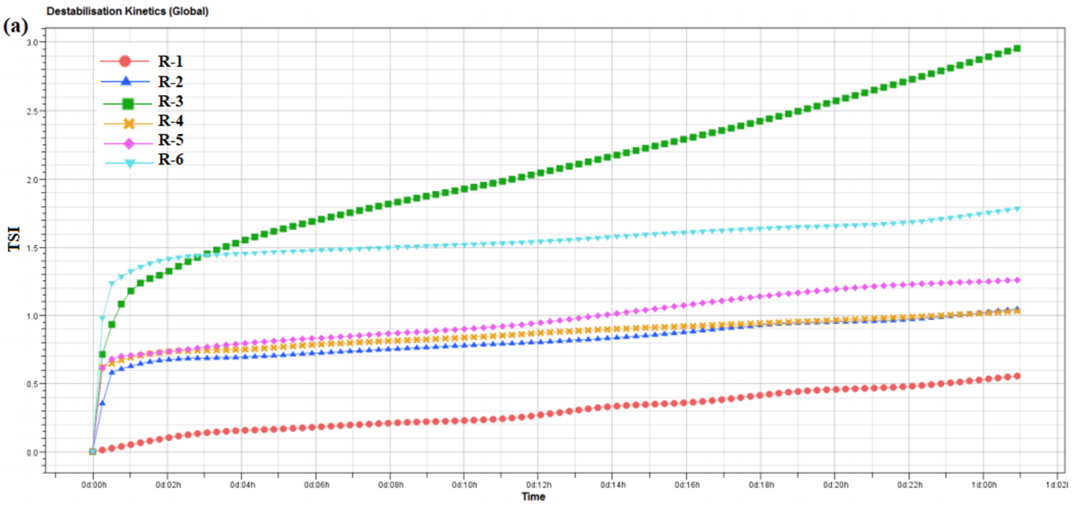

Figure 4.5a: Destabilisation kinetics graphs R-1, R-2, R-3, R-5, R-6.

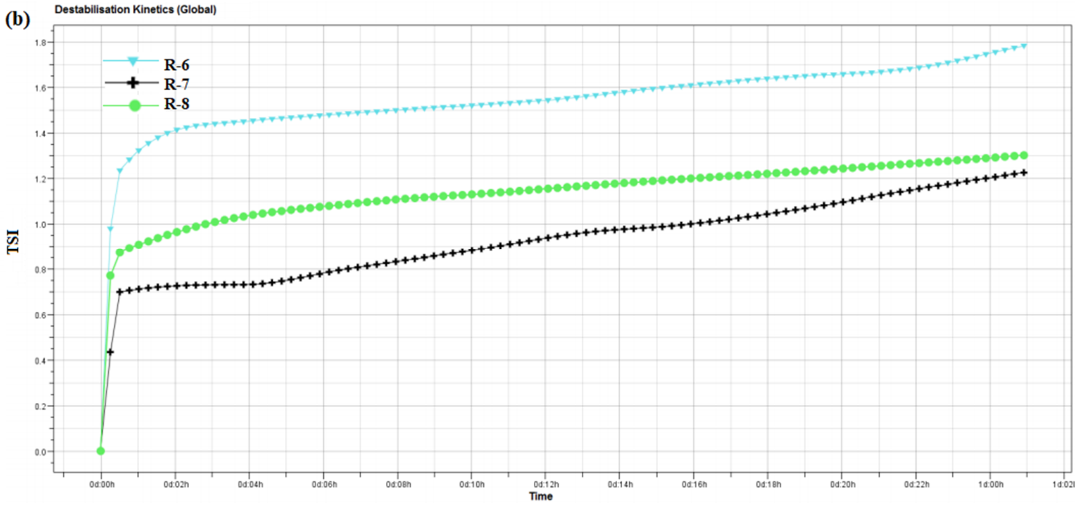

Figure 4.5b: Destabilisation kinetics graphs R-6, R-7, R-8.

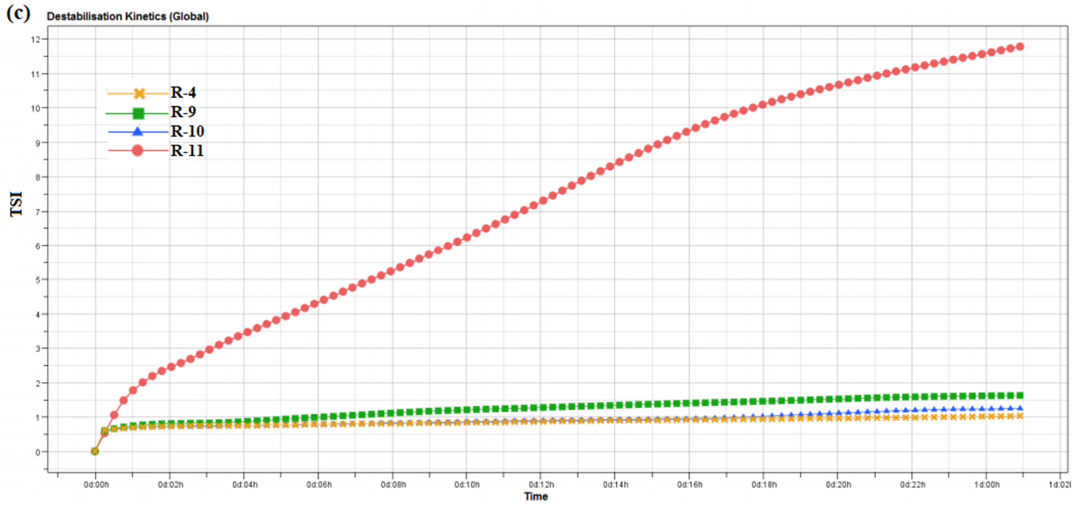

Figure 4.5c: Destabilisation kinetics graphs R-4, R-9, R-10 and R-11.

Table 4.3 : TSI values of 1 day of PUDs, Ac and PU/Ac hybrid disperisions.

Sample Code	TSI (Global) 1 day
R-1	0.5
R-2	1.0
R-3	2.9
R-4	1.0
R-5	1.2
R-6	1.7
R-7	1.2
R-8	1.3
R-9	1.6
R-10	1.2
R-11	11.6

4.2 Properties of Films

The films of Ac emulsion, PUD and PU/Ac dispersions were prepared in silicon molds. For this purpose, dispersions were first poured in the mold and then firstly allowed water to evaporate slightly at room temperature for 48 h. Afterwards, the molds were put in a air circulating oven to allow complete drying for further 48 h at 70 ºC. Film formation ability of synthesized materials are all listed in Table 4.4. All the formed films were all studied by means of thermal and mechanical properties.

Table 4.4 : Film formation ability of PUDs, Ac and PU/Ac hybrid dispersions.

Sample Code	Film Formation (Formed/Not Formed)
R-1	Formed
R-2	Not Formed
R-3	Not Formed
R-4	Formed
R-5	Formed
R-6	Formed
R-7	Not Formed
R-8	Not Formed
R-9	Formed
R-10	Formed
R-11	Formed

4.2.1 Thermal properties

The thermal properties of the films obtained from the synthesized PUDs, Ac and PU/Ac hybrid dispersions were studied by means of differential scanning calorimetry (DSC). DSC thermograms of PUDs′ films from second heating run are shown in Figure 4.6 and the variations of Tg's are presented in Table 4.5. From Figure 4.6, it was observed that there was only one Tg transition arised at low temperature due to the soft segment of polyol and no crystallization and melting peaks were observed providing that reaction was completed as yielding an amorphous polymer. In addition, no phase seperation occurred due to the hard and soft segments in the structure. From Table 4.5, it was concluded by the comparison of the Tg's of PUDs having same NCO/OH ratio (R-4, R-5, R-6) that Tg of the soft segment decreased as the molecular weight of polyol increased owing to decrease in hard segment content. However for the PUDs prepared by using polyols with same molecular weight but different NCO/OH ratios of 1.5 and 2 (R-1 and R-4, respectively), the variation of Tg was found neglible and independent from the NCO/OH ratio.

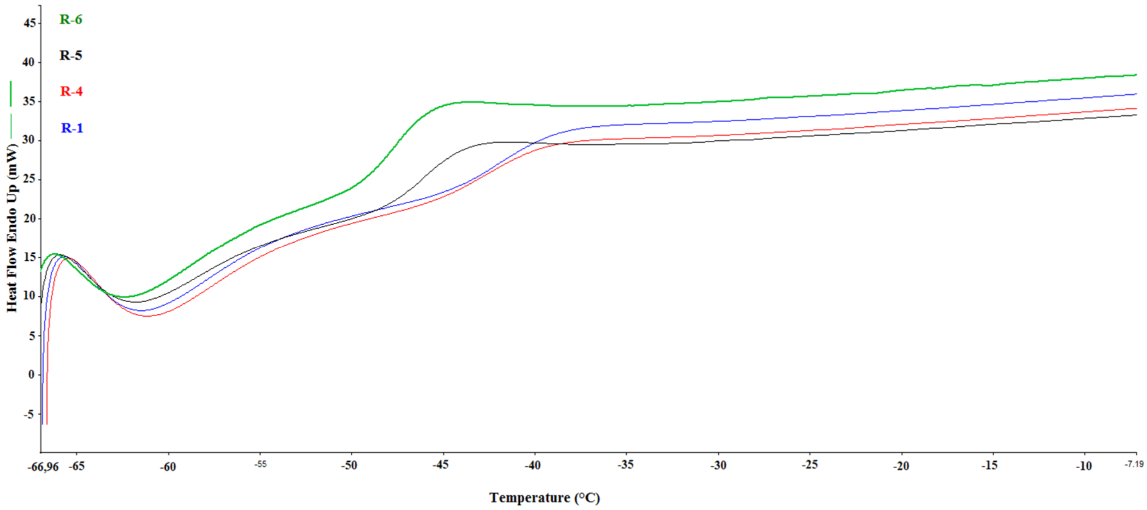

Figure 4.6: DSC thermograms of PUDs' films from second heating run.

DSC thermograms obtained from the second heating run of the of the films of Ac and Ac/PU hybrid dispersions′ are shown in Figure 4.7 and the variations of Tg's are presented in Table 4.5. From Figure 4.7, it was observed that there was only one Tg transition arised at low temperature and no crystallization and melting peaks were observed providing that reaction was completed as yielding an amorphous polymer. From Table 4.5, it was seen that Tg values of films of R-4 (PUD) and R-9 (Ac) were found to be -41.69 °C and -29,69 °C, respectively. It was also observed from the Table that, Tg values of Ac/PU hybrids dispersions' were shifted toward to the Tg value of Ac film with the increase of acrylate content. Accordingly, it was concluded that the arise of one Tg transition and the shiftment of its value proves complete phase mixing of PU and Ac.

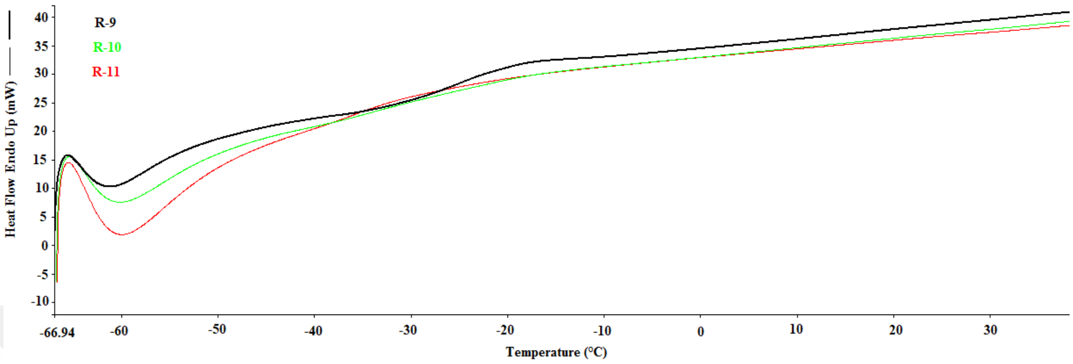

Figure 4.7: DSC thermograms of Ac and Ac/Pu hybrid dispersions' films from second heating run.

Table 4.5 : Thermal and mechanical properties.

Sample Code	**Tg Values (°C)**	σ (MPa)	εp (%)	Shore A
R-1	-40,93	6,422	1240,65	34,5
R-2	-	-	-	-
R-3	-	-	-	-
R-4	-41,69	2,155	75,52	46,2
R-5	-45,45	1,084	300,54	25,1
R-6	-47,09	0,467	478,75	9,7
R-7	-	-	-	-
R-8	-	-	-	-
R-9	-26,95	0,291	1349,25	4,7
R-10	-36,03	1,387	304,63	36,7
R-11	-31,78	1,101	225	33,5

4.2.2 Mechanical properties

The mechanical properties were investigated in terms of shore A hardness and tensile strength of dried films of PUDs, Ac and PU/Ac hybrid dispersions. Tensile strength (σ), elongation at break (ε_p) and shore A hardness values are all listed in Table 4.5. Stress vs strain curve of all films is presented in Figure 4.8.

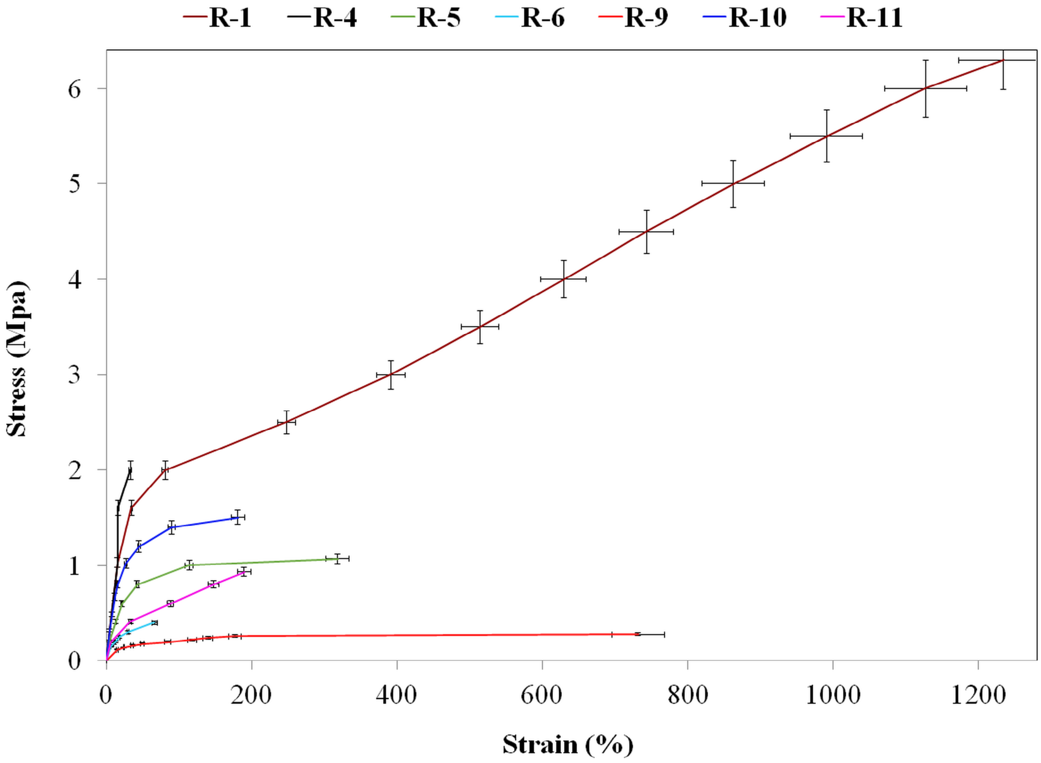

Figure 4.8: Stress vs strain curve of all films.

It was concluded from the comparison of Shore A hardness values of films of the samples R-1, R-4, R-5, R-6 (Table 4.5) that the softness of the films were increased with the increase of the molecular weight of polyol. This result could be atributed to the increment of chain flexibility at higher molecular weight of polyol. On the other hand, it was determined from the comparison of the film properties of R-4, R-10, R-11 samples that, introducing acrylate chains in to the structure led to more softer materials. It was also found that the Shore A hardness decreased with the increase of acrylate content. In addition, the film of R-9 found as the softest film among all others. In coherent with this finding, the film of R-9 showed the lowest tensile strength and highest elongation at break among all films (Figure 4.8 and Table 4.5).

On the other hand, comparision of the elongation at break values and tensile strengths of the films of R-4, R-5, and R-6 showed that with the increase of the molecular weight of polyol, elongation at break of the samples increases while tensile strength decreases. This finding could be explained due to the fact that as the molecular weight of polyol increased, soft segment content increased and hard segment content decreased. As a result of decrement of hard segment, hydrogen bonding between ionic center and urethane linkages decrease and this has resulted in decrement of tensile strength and increment of elongation. However, R-4 has been expected to have the highest tensile strength as compared to R-1, depending on the higher NCO / OH ratio. However, the results obtained show the vice versa. This result might be contributed to comparison of homogeneity of both films: R-1 have formed more homogeneous network than R-4, resulting in high tensile strength and elongation at break [37]. It was concluded from the comparison of film properties of R-4 with R-10 and R-11 that while contribution of acrylate moiety on PU structure led to decrease of tensile strenght, it also increases the elongation at break. However, the increment of acrylate content was found to lead further decrement in tensile strength and elongation at break as a result of weaker mechanical property of Ac unit on the PU chain.

4.3 Properties of Coating

All the synthesized materials were successfully coated on fabrics and some pieces of fabrics were washed after coated in order to see softness together and glossiness on black fabric and pigment binding properties on white fabrics. All these properties were well discussed below mentioned subtitles, respectively.

4.3.1 Softness and glossiness properties

Softness and glossiness properties of the coated fabrics are shown in Table 4.6. In the Table softness and glossiness properties were all graded from 1 to 5, and the properties are increasing as the number increased. It can be concluded from the comparison of coated fabrics (comparison of grade numbers of R-1, R-2 and R-3 coated fabrics within theirselves and R-4, R-5, and R-6 coated fabrics within theirselves) that the softness of all coated fabrics increases with the increase of the molecular weight of polyol,. This results might be attributed to the ratio of hard and soft segments in PU chains. As the molecular weight of polyol increases, the ratio of hard segment amount decreases and flexibility of PU chain increase.

On the other hand, for the glossiness property NCO/OH ratio was seem to be crucial with respect to obtained results. From the comparison of R-1 coated fabric with R-4 coated fabric, it was determined that glossiness increased 1 more point with increase of NCO/OH ratio. In addition to this, once the NCO/OH ratio was constant at 2.0, glossiness was found to increase significantly with the increase of the molecular weight of polyol. Furthermore, coated fabric with R-6 was found to be most glossy material among all PUD samples. From comparison of R-6, R-7 and R-8 coated fabrics, it was found that as the ionic center increased, glossiness decreased but softness did not change. This could be attributed to non-film forming ability as a result of lower molecular weight of PU. Besides that, R-9 coated fabric was also found to show excellent glossiness and softness property as compared to the R-6 coated fabric. It was determined from comparison of the R-4 coated fabric with R-10 and R-11 coated fabrics, with the increase of acrylate content in the polymer chain, glossiness was found to decrease while softness increased. This could be due to the incorporation of acrylate monomers in the hard segment of resulted polymer and increment of hard domains along the polymer chain. Consequently, glossiness property of the fabrics coated with hybrid dispersions decreased.

Table 4.6 also shows the gradings for after washing (A.W.) properties of coated fabrics with respect to softness and glossiness. Accordingly, coated fabrics with R-9 and R-10 kept their glossiness property as 1 point lesser than their before washing form whereas all the other coated fabrics lost their glossiness properties after washing. With respect to softness properties, all coated fabrics with R-1, R-2 and R-3 lost their softness properties as a result of having no washing durability of materials. However, coated fabrics with R-4, R-5, R-6, R-7 and R-8 kept their softness properties as 1 point less than their non-washed forms. On the other hand, it was determined that all of the fabrics coated with acrylate emulsion and hybrid dispersions exhibit wash resistance.

Table 4.6 : Softness and glossiness properties of coated black fabrics

Sample Code	Softness*	Softness A.W. *	Glossiness*	Glossiness A.W. *
R-1	2	1	2	1
R-2	3	1	1	-
R-3	4	1	1	1
R-4	3	2	3	1
R-5	4	3	4	1
R-6	5	4	5	1
R-7	5	4	1	-
R-8	5	4	1	-
R-9	5	5	5	4
R10	3	3	3	2
R-11	4	4	1	-

* 5: Excellent, 4: Very Good, 3: Good, 2: Poor, 1: Very Poor

4.3.2 Pigment binding properties

In order to determine pigment binding properties of all dispersions and emulsion, Data Color 600 instrument was used to measure the color yield. However, due to the partial removal of red pigment with washing, DATA Color measurement could not be applied and the appearance of after washed forms′ of the fabrics were evaluated only visually. CIE Lab values, which were obtaiend from the original software of Data Color, were used to determine differences of colors obtained from different materials synthesized. In CIE lab system, DL* value represents the dark-light axis, Da* represents the green-red axis and Db* represents the blue-yellow axis. DL*, Da* and Db* values obtained from DATA Color instrument of coated fabrics are all listed in Table 4.7. Images of pigment coated fabrics and their after wash forms are presented in Figure 4.9.

Table 4.7 : CIE lab color difference of PUDs, Ac and PU/Ac hybrid dispersions.

Sample Code	**CIE Lab Values**			
	Illuminant	**DL***	**Da***	**Db***
R-1	D 65 10 deg		Standart	
R-2	D 65 10 deg	1,89	-1,60	-4,09
R-3	D 65 10 deg	-0,12	1,52	2,85
R-4	D 65 10 deg	-0,07	0,99	1,76
R-5	D 65 10 deg	-0,17	0,19	1,40
R-6	D 65 10 deg	-0,30	0,68	2,57
R-7	D 65 10 deg	1,69	-1,63	-3,69
R-8	D 65 10 deg	2,49	-2,21	-5,00
R-9	D 65 10 deg	-2,08	0,98	4,23
R-10	D 65 10 deg	-1,13	1,07	3,87
R-11	D 65 10 deg	-0,98	0,50	2,71

L* - the lightness coordinate,with + L* indicating light, and - L* indicating dark.

a* - the red/green coordinate, with +a* indicating red, and -a* indicating green.

b* - the yellow/blue coordinate, with +b* indicating yellow, and -b* indicating blue.

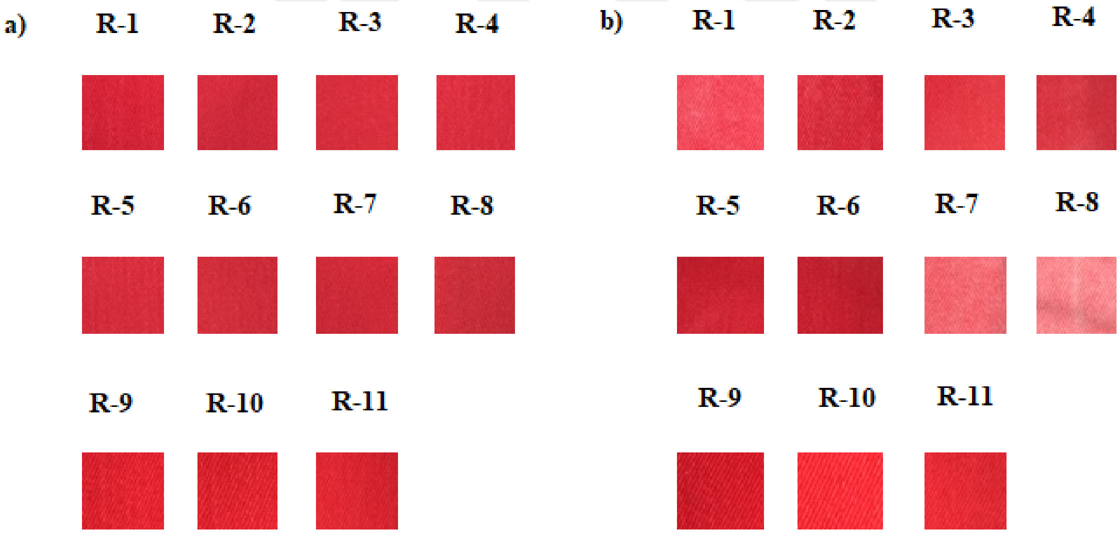

Figure 4.9: Images of pigment coated fabrics (a), their after washing forms (b).

From Table 4.7, with respect to pigment coated R-1 reference fabric, the comparison of R-2, and R-3 in theirselves, R-4, R-5, R-6 in theirselves and R-1 with R-4; R-2 with R-5; and R-3 with R-6 showed that the lightness of the color of fabrics decrease with the increase of the molecular weight of polyol while the NCO/OH was constant. The same influence was also observed, when the NCO/OH ratio of the dispersions was increased but the molecular weight of polyols were constant. Moreover, it was also observed that among the pigment coated fabrics with R-1, R-2, R-3, R-4, R-5, and R-6, pigment coated fabric with R-2 was showed more green and more blue appearance.

The pigment coated fabric with R-3, on ther hand, was showed more red and more yellow appearance. From comparison of R-6 with R-7 and R-8, it was concluded that as the ionic center increased, lightness of the color of pigment coated fabrics increased and fabrics had more green and more blue appearance. In addition to all, pigment coated fabric with R-9 was determined as the one exhibiting the darkest value among all others. From the comparison of R-4 with R-10 and R-11, it was also concluded that introduction of acrylic moiety in to the PU backbone lead to more darker apperance onto fabrics. However, it was observed that increase in the acrylic content was slighlty decrease the darkness value and lead less red and yellow appearance.

From Figure 4.9, it was obviously seen that pigment coated fabrics with R-7, R-8 showed dramatic color loss after one wash. Moreover, it was observed that the color loss increased with increasing ionic center in PU backbone. It was obviously concluded from comparison of R-1, R-2, R-3 within themselves; R-4, R-5, R-6 within themselves; and R-1 with R-4; R-2 with R-5; and R-3 with R-6 that the color loss decreased with the increasing molecular weight of polyol at constant NCO/OH ratio, and increasing NCO/OH ratio for the PUDs prepared with the same molecular weight polyol. In addition to all, pigment coated fabric with R-9 was found to exhibit washing durability. Moreover, from the comparison of R-10 with R-11, color retention property was found to be improved after one wash with the increasing acrylic moiety in PU backbone.

Table 4.8 : Rubbing Fastness Ratings

Sample Code	**DRY***	**WET***
R-1	2-3	1-2
R-2	2	2
R-3	2	1-2
R-4	3-4	1-2
R-5	4	3
R-6	3	2-3
R-7	1-2	1-2
R-8	2	1-2
R-9	2	4
R-10	4	2
R-11	3-4	2-3

* Evaluation from 1 to 5 where 5 is best and 1 is worst

Elasticity, adhesion property and pigment dispersion ability of binders were recently found to be important factors effecting rubbing fastness properties [173]. In this context, wet and dry rubbing fastness properties of pigment coated fabrics were examined and their ratings are given in Table 4.8. From the comparison of R-1, R-2, and R-3 with R-4, R-5, and R-6, respectively, it was found that dry rubbing fastness of pigment coated fabrics increased with the increase of NCO/OH ratio. This might be explained by better film formation and lower elasticity leaded with the increasing NCO/OH ratio. It was found that, with the ratings of 4 and 3, respectively for dry and wet rubbing fastness, R-5 had exhibited the best dry and wet rubbing fastness property among all PUDs. From comparison of R-6 with R-7 and R-8, dry rubbing fastness was found to decrease with the introduction of more ionic centers onto PU backbone, due to their poor film forming ability and poor washing resistance. Pigment coated fabrics with R-1,R-3, R-4, R-7, R-8 had only 1 or 2 ratings over 5 points, whereas pigment coated fabrics with R-2 and R-6 had exhibited ratings of 2 and 2-3, respectively. Pigment coated fabric with R-9, on the other hand, had a rating of 2 for dry rubbing fastness whereas it has exhibited the highest rating for rubbing fastness with a rating of 4 among all coated fabrics. From comparison of R-10 and R-11, it was concluded that dry rubbing fastness rating decreased and wet rubbing fastness rating increased by half grade as acrylate content increased. The good wet rubbing fastness property might be explained with the hydrophobic nature of acrylate monomers.

5. CONCLUSION and RECOMMENDATION

Since their properties can be finely tuned by changing their components, PUs have a broad range of applications. Their special and versatile properties, including chemical, solvent, and abrasion resistance, flexibility, gloss and toughness, give them both technical and economic importance. However PUs have some disadvantages such as high cost, low pH stability and fair outdoor durability. Preparation of hybrid type dispersions, on the other hand, is a versatile approach for the combination of unique properties of individual polymer chains and elimination of disadvantages of PUs.

In this thesis, anionic waterborne PUDs were prepared by using an ionomer having sulfonate groups (AAS salt) via acetone process. The hybrid dispersions were then obtained by further copolymerization reaction with butyl acrylate (BA) and ethyl acrylate (EA). For this purpose, pre-synthesized PUs were first reacted with an end capping agent, hydroxyl ethyl acrylate (HEA), in order to gain double bond functionality to the PU chains, and then different ratios of butyl acrylate (BA) and ethyl acrylate (EA) were added into the reaction mixture. In addition to PUDs and PU/Ac’s, and an acrylate emulsion was also prepared by using HEA, BA and EA, in order to make a comparision between the final product properties. According to our current knowledge, AAS salt ionic center has not been studied in polyurethane acrylate hybrid dispersions with the use of HEA, BA and EA monomers, yet. Hence, the fabric coating properties of these hybrids have also not been investigated before.

In order to determine their application properties, resulting materials were characterized in terms of their physicochemical, thermal and mechanical properties. Moreover, for the evaluation of influence of obtained materials in textile applications, all materials were applied on cotton fabrics via knife air coating method. Besides that, pigment binding properties were also investigated.

In general, it was found that particle size distribution of the PUDs were found to be variated due to the NCO/OH ratio, molecular weight of polyols and as well as the amount of chain extender and acrylate content. PUDs became more uniformly distributed with the increase of molecular weight of polyol and chain extender amount, and with the decrease of NCO/OH ratio. Moreover, increase in acrylate content was found to lead more uniform distribution.

Considering stability analysis done by Turbiscan Lab, stability of the PUDs were found to be variated due to the NCO/OH ratio, molecular weight of polyols and as well as the amount of chain extender and acrylate content. It could be concluded that PUDs became less stable with the increase of molecular weight of polyol and chain extender, and the decrease of NCO/OH. Furthermore, it could also be concluded that grafting with acrylate monomers resulted in less stable product.

Regarding thermal and mechanical properties, it was observed that there was only one Tg transition arised at low temperature due to the soft segment of polyol and no crystallization and melting peaks were observed providing that reaction was completed as yielding an amorphous polymer. In addition, no phase seperation occurred due to the hard and soft segments in the structure. It was found that for the PUDs having same NCO/OH ratio, Tg of the soft segment decreased as the molecular weight of polyol increased owing to decrease in hard segment content. However, for the PUDs prepared by using polyols with same molecular weight, variation of Tg was found neglible and independent from the NCO/OH ratio. It was also determined that Tg values of Ac/PU hybrids dispersions′ were shifted toward to the Tg value of Ac film with the increase of acrylate content. Accordingly, it was concluded that the arise of one Tg transition and the shiftment of its value proves complete phase mixing of PU and Ac. According to Shore A hardness values, the softness of the films were increased with the increase of the molecular weight of polyol and acrylate content. On the other hand, comparision of the elongation at break values and tensile strengths of the films showed that with the increase of the molecular weight of polyol, elongation at break of the samples increases while tensile strength decreases. In addition, it was found that contribution of acrylate moiety on PU structure led to decrease of tensile strength, and increases the elongation at break. However, the increment of acrylate content was found to lead further decrement in tensile strength and elongation at break.

Regarding textile application, it can be generally concluded that the softness and glossiness of all coated fabrics increase with the increase of the molecular weight of polyol and NCO/OH ratio. However, with the increase of acrylate content in the polymer chain, glossiness was found to decrease while softness increased. It was also determined that all of the fabrics coated with acrylate emulsion and hybrid dispersions exhibited wash resistance. According to data color analysis, it was concluded that the lightness of the color of fabrics decreased with the increase of the molecular weight of polyol and NCO/OH ratio and, as well as the decrease of ionic center. Furthermore introduction of acrylic moiety in to the PU backbone was found to led to more darker appearance onto fabrics. Yet, it was observed that increase in the acrylic content slighlty decreased the darkness value. On the other hand regarding to washing durabilities, it was observed that the color loss increased with increasing ionic center in PU backbone and decreasing molecular weight of polyol and, increasing NCO/OH ratio. Moreover, color retention property was found to be improved after one wash with the increasing acrylic moiety in the PU backbone. Dry rubbing fastness of pigment coated fabrics was found to increase with the increase of NCO/OH ratio and decrease with the introduction of more ionic centers and acrylate moeity onto PU backbone, in addition most PUDs showed poor wet rubbing fastness this property was proved to be improved with the introduction of acrylate moeity.

There are great number experiments, tests and applications that can be done in this field. For this reason, I would like to share some recommendations for future work. GPC analysis and NMR spectroscopy could be utilized to assess synthesis and grafting properties of PUDs and PU/Ac hybrid dispersions. Chemical resistance properties and morphology analysis of films could be also studied. Moreover, the application of hybrid dispersions in other coating industries like wood, leather, and etc. could be also investigated. Different kinds of polyols (OH) and isocyanates (NCO), available in the market, could be formulated with different combinations and final properties for the same application could be studied

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CURRICULUM VITAE

Name Surname: ÖZNUR EMEKLİOĞLU

Place and Date of Birth: KARŞIYAKA 06.07.1988

Address: ALTINKOZA 2 SİTESİ 3 A BLOK DAİRE 5 ZÜMRÜT SOKAK FSM
MAHALLESİ EMEK OSMANGAZİ/BURSA

E-Mail: oznurmalatyali@gmail.com

B.Sc.: CHEMISTRY

M.Sc. (If exists):

Professional Experience and Rewards:

R&D Specialist in textile auxiliaries.

List of Publications and Patents:

PUBLICATIONS/PRESENTATIONS ON THE THESIS

- Emeklioğlu Ö., Mert E. M.., Yavuz Ö. N 2018: Synthesis of Anionic Waterborne Polyurethane and Acrylate Grafted Polyurethane Dispersions for Textile Coating Applications. *EurasianBioChem 2018.* April 26-27, 2018 Ankara, Turkey.
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