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NMP free hybrid polyurethane dispersions as adhesive for plastic laminates

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ABSTRACT

Anionic polyurethane dispersions (PUDs), with and without butyl acrylate modifications were synthesized using polypropylene glycol, and/or monoglyceride of castor oil as polyols. The synthesized PUDs were analyzed by FTIR, MFFT and particle size analysis. These dispersions were tested for its contact angle with liquids having ringed of polarities. Further these dispersions were employed as an adhesive and were evaluated for its peel strength for LDPE and PET laminates.

Keywords: Emulsion polymerization, polyurethanes, adhesives, graft copolymers, SEM

INTRODUCTION

From yester years, polyurethane dispersions (PUDs), have begun to show its charisma in the application areas namely surface coating etc, previously dominated by solvent borne systems, for two important reasons. First, environmental concern, solvent emission in the atmosphere causing ozone depletion leading to global warming, while the second is economic involved for organic solvent as systems based on organic solvent are expensive. Although performance of the aqueous systems has to be improved to the point that are comparable or better than the conventional solvent-based polyurethanes (PUs). [1]

One of the prevailing variant of water borne polyurethane are the low volatile organic compound (VOC) polyurethanes, possessing small amount of co-solvent, inducted as a processing aid with the additional benefit of coalescing and the dispersion of the particles into a smooth, continuous film for this N- Methyl-2-Pyrrolidone (NMP), has been the choice. NMP is an expensive and has a strong tendency to oxidize, moreover, NMP residue in the dried film tends to cause yellowing and capable of dissolving or swelling a wide spectrum of protective gears in an industrial environment. With reference to one of the California Propositions, all products containing NMP require special labeling, describing the amount of NMP contained in it. [2]

NMP free PUDs, needs to be customized to offer high performance in terms of combination of toughness, abrasion resistance, flexibility and chemical resistance.[3] NMP free PUDs have drawbacks of high cost, low pH stability and limited outdoor durability, whereas acrylic emulsions have an excellent weather resistance, good pigmentability and lower cost. In order to reduce cost/performance balance, acrylic emulsions have been incorporated into the PUDs. [4, 5] Physical blend of acrylic emulsion and PUD results in films composed of distinct phases of two polymers as there is very limited compatibility between them. Kukunja *et. al.*[4] had compared the performance of Acrylic-Polyurethane hybrid emulsions with physical blends and found that hybrid emulsions provide improved performance in coatings. Hirose and Kadowaki used core-shell polymer obtained from aqueous dispersions.[7] Interpenetrating polymer network, IPN was prepared using acrylic monomers polymerized in presence of the PUDs. [6] Hourston *et. al.*[8] has reported the mechanical properties and morphology of PU/PS IPNs for coating applications. Brown *et. al.* had compared the performance of the acrylic-PU hybrid emulsions with corresponding blends of PU and acrylic emulsions for coatings. Acrylic emulsions were the copolymer of MMA/BA/AA and PUD were anionically stabilized aliphatic, polyester based containing NMP co-solvent.[6] Sebenik *et. al.*[9] has synthesized acrylic-PU hybrid emulsions by polymerization of various acrylic monomer mixtures like BA, MMA and AA in presence of PUD, which was anionically stabilized, consisting of aliphatic polyester carbonate in NMP medium. The mechanical properties of emulsions, prepared by varying weight ratio between acrylic and PU components were compared.[9] Most of the work reported on acrylic-PU hybrid emulsion is in the form of patents.[13, 16–19, 24, 25] which have potential for the application in the field of coatings and only a few publications are available showing systematic study.

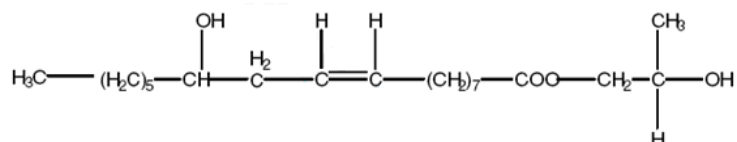
The commercially available PUD contains 15-26% NMP as a cosolvent, acrylic components were mixture of various acrylic emulsions made from BA/MMA/AA monomers, all dispersions have the potential for use in the field of coatings. No work has been reported to show the consequence of the acrylic components on the PU backbone and their use as adhesives for flexible packaging laminates. Fast depleting petroleum derived products are forcing us renewable resource, like castor oil can be useful source. In the present study, castor oil was used to prepare monoester by the process of alcoholysis. This monoester were used as a polyol in the preparation of PUDs, of these batches some were modified with n-BA monomer, while others were kept unmodified and diluted with NMP solvent these batches were then compared for its effectiveness as adhesive for plastic laminates.

MATERIALS AND METHODS

Castor Oil [Jayant Oil Mills Ltd. India], 1,2 – Propanediol, Triethyl amine (TEA), Ethylene diamine (EDA) as a chain extender, N- Methyl-2- Pyrrolidone [Merck, Germany] , Isophorone Diisocyanate (IPDI) [Degussa, USA], Polypropylene glycol (PPG Mw=2000}[Manali Petrochemicals, India], Dibutyl tin dilaurate (DBTL) [Dura chemicals, India], Butyl Acrylate (BA) [National chemicals, India], Azo Bis Iso butyro nitrile (AIBN), were used without purification and Dimethylol Propionic Acid (DMPA) [Perstop Co. India] was vacuum dried at 80 – 85⁰C before use. PET and LDPE films were obtained from Mittal Industries, India.

Synthesis of 2 – hydroxyl propyl ricinoleate (2 – HPR)

Along with 0.3 % of dry sodium hydroxide, based on the mole of the castor oil. The molar ratio of propanediol to castor oil was 9:1 .The reaction mixture was stirred at room temperature for one hour, after that it was allowed to stand overnight. Resultant 2-HPR was purified by water washing. 2–HPR has hydroxyl value 313 mg of KOH per gram of sample, the structure of 2-HPR is shown in Figure-1.

Figure 1 Structure of 2 – HPR**Synthesis of Urethane Prepolymer**

The recipes for the synthesis of PUDs are presented in the Table- 1. A clean, dry glass reactor equipped with a stirrer, condenser, nitrogen inlet, and thermometer charged with the calculated amount of reactants, BA monomer (25% of the total solids) containing sufficient inhibitor and urethane catalyst DBTL (0.03% based on total solids). The reaction was allowed to proceed at 80⁰C to obtain NCO terminated prepolymer. The reaction monitored by measuring –NCO value by dibutylamine back titration method [10]. Upon achieving the theoretical NCO values, calculated from the [NCO]/ [OH] index of feed, the prepolymer was cooled to 60⁰C. The batch with cent percent, HPR contained high functionality was gelled and thus not considered for the adhesive applications.

TABLE–1: Recipe for the synthesis of Acrylic–Polyurethane hybrid dispersions.

Sr. No.	Component	No. of Moles					
		PU-1	APU-1	PU-2	APU-2	PU-3*	APU-3*
1.	IPDI	0.535	0.535	0.535	0.535	0.535	0.535
2.	DMPA	0.178	0.178	0.178	0.178	0.178	0.178
3.	PPG-2000	0.148	0.148	0.073	0.073	--	--
4.	2-HPR	--	--	0.073	0.073	0.148	0.148
5.	NMP	15 % of Total Solids	--	15 % of Total Solids	--	15 % of Total Solids	--
6.	n-BA	--	25 % of Total Solids	--	25 % of Total Solids	--	25 % of Total Solids
7.	TEA(g)	19.00	19.00	19.00	19.00	--	--
8.	Distilled Water(g)	714.00	958.00	552.00	683.00	--	--
9.	EDA (g)	6.00	6.00	6.00	6.00	--	--

* = PU-3 and APU-3 batches gelled

PU-1 = Polyurethane dispersion based on PPG-2000 in NMP cosolvent

APU-1 = Acrylic-polyurethane hybrid dispersion based on PPG-2000

PU-2 = Polyurethane dispersion based on PPG-2000 and 2-HPR in NMP cosolvent

APU-2 = Acrylic-polyurethane hybrid dispersion based on PPG-200 and 2-HPR

PU-3 = Polyurethane dispersion based on 2-HPR in NMP cosolvent

APU-3 = Acrylic-polyurethane hybrid dispersion based on 2-HPR.

Emulsification and Chain Extension

In this prepolymer/monomer mixture was dispersed with high-speed agitation into distilled water contains stoichiometric amount of TEA for neutralization of residual acids of DMPA. The free isocyanate functionality was utilized with chain extender EDA, to give rise to polyureas.

Preparation of Hybrid Emulsion

The PUD-BA monomer mixture, AIBN oil soluble free radical initiator was added and heated at 75°C under nitrogen blanket for BA polymerization. During the reaction, part of the BA gets grafted onto the PU backbone, while the remaining BA homopolymerize in the dispersion to form IPN. While unreacted BA in the PUD, acts as a solvent and helps in controlling the viscosity during film formation and hence avoiding use of any other cosolvent. Hence the resultant acrylic-PU hybrid emulsions provide the advantages of zero VOC over conventional PUDs.

Laminates Preparation

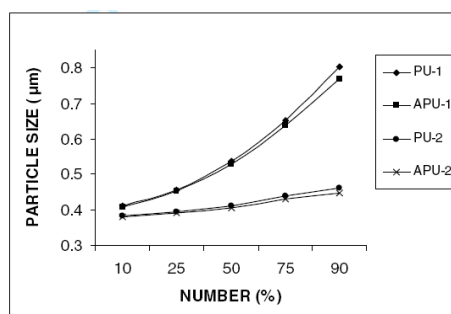
LDPE films were corona treated, for surface tension of 34 dynes/cm and PET films were cleaned with isopropyl alcohol solvent prior to lamination. The adhesives were applied onto the treated side of the one substrates with the help of bar coater depositing wet film of 24 micron thickness. The coating was then preferably exposed to microwave radiation for one minute at 60 – 85°C for the complete removal of water and unreacted BA. Second substrate was applied onto the adhesive film of first substrate by under pressure of 260Kg/ m². The laminates were carefully cut to produce a centrally deposited 25 mm wide band and the lateral bands specimens were removed to avoid any edge effects. These strips were then tested for peel strength.

Characterization

Particle Size Analysis

The particle size was determined using particle size analyzer (Coulter LS, Japan). The particle sizes for hybrid PUDs are as shown in Figure – 2.

Figure 2 Particle size Vs Number %



Contact Angle

Contact angle was measured on DIGIDROP contact angle meter. Instrument with specimen Dimensions: 700 x 350 x 290 (mm), angle range from: 0° to 180°. Software with of contact angle: +/- 0 to 2° accuracy with the ADSA method,

FTIR Analysis

Infrared (IR) Spectra of 2-HPR and PUDs were recorded using Fourier Transform Infrared (FTIR) Spectrometer (SHIMADZU, model 8400-S, Japan). The films were subjected to FTIR analysis at 4 cm⁻¹ resolution in the mid-IR range, from 4000 to 400 cm⁻¹. The graphs are shown in Figure no.4, 5 and 6.

Peel Strength

Instron tensile testing instrument parting at a speed of 30 cm/min. Bond strength was measured by a Peel Test according to ASTM D 1876-72

Table 3 Peel strengths (g/cm) for various substrates for different PU adhesives

Sample	PET-PET	PET-LDPE	LDPE-LDPE
PU-1*	10	10	18
APU-1*	14	38	18
PU-2	30	10	42
APU-2	118	68	100

Grafting Efficiency Solvent Extraction Method

The grafting efficiency of sample was determined by a solvent extraction method. This method involved adding 1.0 g of casted polymer film, in 100 mL toluene and mixing for 24 h, with end-over-end tumbling at room temperature. The weight of dissolved polymer was determined from the solids content in the supernatant.

Minimum Film Forming Temperature (MFFT)

Minimum film forming temperature of all the hybrid emulsions were characterized for its minimum film forming temperature with the help of MFFT detector (CIPET, India). All the values were falling below 5⁰C and finding the MFFT below this temperature was beyond the scope of this instrument.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) of all the samples were characterized for its morphology with the help of Analytical Scanning Electron Microscope Jeol JSM-6380LA Japan.

RESULTS AND DISCUSSION**Adhesive Performance**

In case of PUDs, prepared from polyether polyol i.e. PPG 2000 containing NMP and BA were completely free from unstaurations in the polymer backbone. In case of NMP cosolvent, NMP helps in enhancing the flow and leveling of the adhesive films and thus imparting better film forming property, but it has very poor adhesive property .In BA cosolvent case, this monomer also acts as reactive diluents, this in presence of free radical initiator polymerizes in presence of PU resulting into IPN. In these IPNs, both the polymers retain their individual identity and remain as two separate phases. This heterostructure is hardly of any use from the adhesive view point and therefore the adhesive perform poorly in all the plastic laminates as mentioned in figure no.3. In case of PU prepared with equal weight fractions of polyether polyols and polyester polyols i.e. PPG 2000 and 2-HPR, this polymer contains unstaurations in the polymer

backbone contributed by 2-HPR. HPR which has molecular weight ten times lower than PPG 2000 and containing two hydroxyl groups of that one is primary while the other one is secondary. This may results into a low molecular weight urethane prepolymer. When BA was polymerized in presence of unsaturated polymer, it has the tendency to form a graft copolymer and it was evident from the grafting efficiency. The ultimate structure resembles like a comb structure consisting of PU chains adhering to the substrate while the graft chain radiating out as tentacles. These tentacles are acting as pressure sensitive points in holding the second substrate providing good peel strength.

Grafting Efficiency (GE)

When the grafting efficiency of APU-1 and APU-2 consisting of saturated and unsaturated backbone, with BA cosolvent was zero and 86% respectively which imply that BA has got no tendency to graft on PPG backbone, whereas it has highest for unsaturated HPR.

FTIR Analysis

The IR Spectrum of 2 – HPR shown in the Figure 4. The presence of characteristic peak at 3540 and 3443 cm^{-1} shows the presence of – OH group and the peaks at 3060 and 3010 cm^{-1} shows the presence of unsaturated –CH bond. The stretching of methyl group is shown by the presence of peaks at 2970 and 2870 cm^{-1} . The presence of peak at 910, 902 show the presence of $-\text{CH}_2$ of terminal methylene group. The IR Spectrums of PU-1, APU-1 are shown in the Figure 5, while the spectrums of PU-2 and APU-2 are shown in Figure 6. Almost all the infrared research on PU has been focused on two principal vibrational regions: the $-\text{NH}$ stretching (3360 cm^{-1}) and $\text{C}=\text{O}$ stretching (1700-1730 cm^{-1}). Dried films showed no peak at 2270 cm^{-1} which indicates the absence of free NCO and hence the completion of reaction. Clearly in APU-1 and APU-2 shows peak at 725 ~ 720, which shows the presence of long chain n-alkyl compounds obtained after the polymerization of n-BA. As PU-1 and PU-2 are unmodified PUDs in NMP, they lack the peak at 725 ~ 720. Moreover, as compared to PU-1 and PU-2, in other sets APU-1 and APU-2, the areas under the peak at 2960 cm^{-1} (for stretching C-H Bond) increased which also confirms the presence of long chain n-alkyl compounds. The presence of broad band at 1080 cm^{-1} in case of PU-1 and APU-1 show that they are polyether based PU.

Figure 4 FTIR Graph of synthesized 2 – HPR

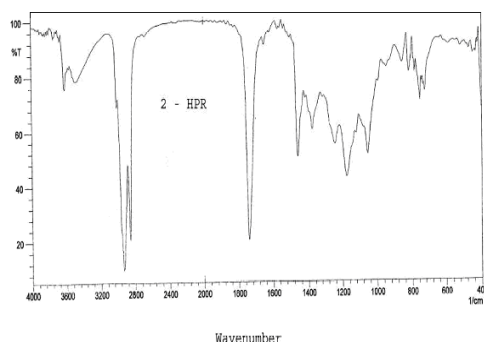
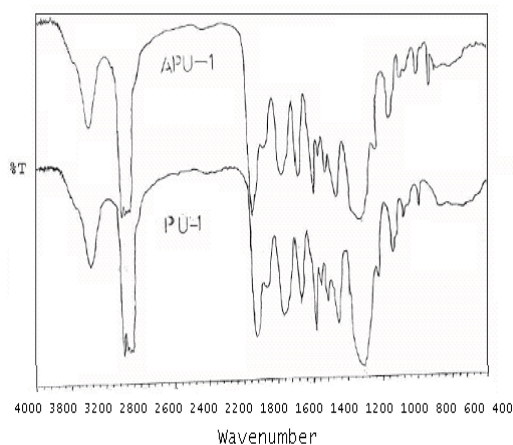
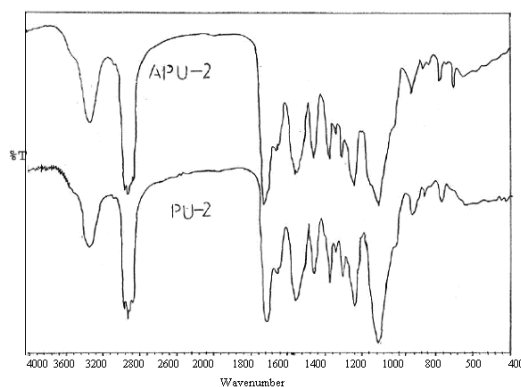


Figure 5 FTIR graph of PU -1 and APU - 1**Figure 6 FTIR graph of PU -2 and APU -2**

Contact Angle

Surface tension of LDPE is lower than that of PET and therefore wetting of LDPE would be difficult task. Contact angle of all the liquids i.e. water, low molecular weight PET and liquid paraffin is lower than 90° , therefore wetting is spontaneous. Although paraffin oil is good at the wetting because of the lower contact angle compare to other two. This indicates that somewhat orientation of BA chains seems to be responsible. The other two polar liquids i.e. water and low molecular weight PET are having relatively high contact angle are bound to face difficulty in spreading & wetting the substrate. PU-1 and 2 are better in low contact angle, although PU-1 is the best in wetting for non-polar whereas PU-1 for polar liquids for wetting the substrate.

TABLE - 2 Contact angle of PU for different liquids

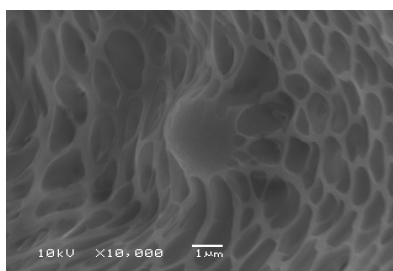
Sample	Contact Angle ($^{\circ}$)		
	Water	Low Molecular Weight PET	Liquid Paraffin
PU-1	60.4	34.56	36.54
PU-2	70.6	48.34	39.60
APU-1	68.4	60.56	28.56
APU-2	81.6	63.45	40.53

Scanning Electron Microscopy (SEM)

Free carboxylic groups of DMPA present as a pendent groups on PU backbones were neutralized with TEA and dispersed in water to form PUDs. BA added to these PUDs, enters into the micelles, because of its hydrophobic nature. When these PUDs subjected to heat and in presence of initiator, it polymerizes BA, part of BA grafted on the PU backbone and the remaining homopolymerized to PBA, to form IPN.

In a morphology, the central globule of PU grafted with BA chains, are appearing as tentacles originating from the core and the hallow portion representing PBA uniformly distributed, providing a clear evidence of IPN shown in Figure 7.

Figure7. The SEM morphology of the hybrid dispersion



CONCLUSION

Single component waterborne, high performance, hybrid acrylic-urethane have been synthesized to offer cost/performance advantages over standard single component polymeric materials such as PUDs, acrylic emulsions, and blends thereof. Day by day, the prices of petroleum are increasing and consequently the prices of petroleum derived products like polyether polyol, etc. are rising. So here a low cost castor oil based monoester (2 – HPR) has been formed and incorporated as a polyol component the PU to form low cost PUDs with acrylic modification. The NMP-free hybrid dispersions have been shown to provide adhesion properties higher than their NMP-containing counterparts. This acrylic modified PUDs based on castor oil showed good potential for use as laminating adhesives for flexible packaging industries in combination with polyether polyol. Due to the lack of NMP and low residual monomer contents, NMP-free hybrid dispersions were observed to have reduced odor, which is obviously desirable from a health and safety perspective. In addition, the lack of NMP offers potential regulatory benefits (e.g., California Proposition 65). For PET/PET, PET/LDPE and LDPE/LDPE laminates, the system with 50% PPG – 2000 and 50% 2-HPR modified with 25% n-BA offered best results as an adhesive. Thus, the castor oil modified systems with acrylic modification has good potential as lamination adhesives for flexible packaging industries.

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