

Highly Branched and Tartaric Acid-Based Water-Borne Resins

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ABSTRACT: In this study, water-borne polyurethane resins were produced using poly(propylene-ethylene) copolymer triol, toluene diisocyanate, and hydrophilic monomers, dimethylol propionic acid and tartaric acid. The hydrophilic monomers were used separately. In either case, the ratio of isocyanate functional groups to the sum of hydroxyl groups of polyol and hydrophilic monomer was kept constant. The increase in the amount of hydrophilic monomer increased the hardness of resins when used as varnish. Tartaric acid resulted in higher hardness than dimethylol propionic acid. The dispersions made by using tartaric acid had much larger particle sizes than those of dimethylol propionic acid. In another set of experiments, the samples carrying the optimum properties from the two sets were mixed with methylol urea that served as crosslinker in the baking step. The physical and mechanical properties were determined by changing the weight percentages of the two types of samples in the mixture, and by changing the methylol urea percentage of the mixture which exhibited the maximum hardness. All samples showed superior impact resistance, adhesion, and flexibility. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 604–612, 2001

Key words: water borne; tartaric acid; dimethylol propionic acid; toluene diisocyanate

INTRODUCTION

Polyurethanes (PUs) were invented in 1937, and since then, they have been developed to an extensive and useful class of polymers. Their unique property is that they contain a “soft” segment, usually made from a polyether or a polyester, and a “hard” segment which contains a urethane unit from reaction of an isocyanate and a diol or triol.

A wide variety of PUs with a broad spectrum of desirable properties can be synthesized by using appropriate monomers. Soft segments and hard segments differ not only in hardness and flexibility, but also in polarity, interchain interaction, and compatibility. In a typical PU elastomer, the soft segments comprise more than 50% by weight of the polymer and form a continuous matrix. The hard segments aggregate and form microdomains with enhanced cohesion and act as pseudo-crosslinks.

The incorporation of ionic sites in the form of ionomers causes PUs to have very interesting properties. The ionic groups, polarity, and coulombic forces in various urethane ionomers result in many interesting applications. The water-

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borne products have begun to substitute solvent-borne polymeric resins in the paint industry. The ionic groups on the backbone or on the pendant chain bring about ionic aggregation resulting in different morphologies. When the ionic groups are turned into internal salt groups, it becomes possible to obtain water dispersability that is utilized in making water-borne resins and adhesives. The combination of high/low polarity, hard/soft segments, and hydrophobic/hydrophilic structures result in novel water-borne resins. Water-borne resins have already partially replaced some of the solvent-borne resins and in near future new formulations will be developed, and most of the solvent-borne resins will disappear from the market. There is a large amount of research on water-borne resins to minimize the use of solvent-borne resins, and thus to have a less polluted environment.

The aim of this research was to prepare a new water-borne resin starting from raw materials easily available in the market, especially poly(propylene-ethylene) copolymer triol (PO), and tartaric acid (TA), and to show the dispersion property of the products obtained. The polyols used in such resins are usually linear polyester polyols. However, PO is one of the most available polyols on the market. In addition, dimethylol propionic acid (DMPA), mostly used in the research of such resins, has not yet been much commercialized, and TA may introduce better properties to resin than DMPA. The carboxyl groups of TA are less sterically hindered than that of DMPA, and it may yield some branching. The use of polyether polyols may compensate for the loss in flexibility due to branching. To compare the effects of TA and DMPA, different resins were prepared with both TA and DMPA at different acid/polyol concentrations and their emulsification properties, and physical and mechanical properties were investigated. In addition, two different resins containing DMPA and TA were blended and cured with dimethylol urea that acts as crosslinking agent.

WATER-BORNE PU

The polyols used in PU elastomer synthesis are of polyethers, polyesters, polycaprolactone, and polycarbonate origine.¹⁻⁷ Polyesters have some advantages over polyethers with respect to strength, oil resistance, etc. Polyols used are either linear or slightly branched. Short chains re-

sult in greater number of urethane links and thus different physical properties.

Nearly any type of di- and/or higher functionality isocyanate can be used in PU dispersions.^{1,3-7} The important point is that the isocyanate must exhibit sufficient stability toward water during processing so that urethane bonds must form instead of urea bonds. However, only several diisocyanates are used commercially, such as toluene diisocyanate, diphenylmethane diisocyanate, isophorone diisocyanate, hexamethylene diisocyanate, etc. Aromatic isocyanates, which had been neglected in earlier stages of PU dispersion chemistry are nowadays used in some newly developed techniques. Processing is preferably performed below 10°C to minimize formation of urea groups.⁷ The blocking of isocyanate (NCO) groups at the end of prepolymer molecules with a blocking agent is a useful technique to prevent isocyanate-water reactions during dispersing operation.⁸

The relative reactivity of the NCO group with other groups can be placed in the following order⁹: aliphatic NH₂ > aromatic NH₂ > primary OH > water > secondary OH > tertiary OH > phenolic OH > COOH and, R-NH-CO-NH-R > R-CO-NH-R > R-NH-COO-R.

The PU chains with NCO terminating groups can be extended with diamines forming urea groups. This gives advantageous properties to PUs. The isocyanate-water reaction is minimized during the production of high performance PU dispersions because the carbon dioxide evolution in this reaction causes severe foaming. Because the NCO + NH₂ reaction is faster than the NCO + H₂O reaction, it is possible to accomplish chain extension with diamines.¹⁰ The aliphatic amines are preferred over the aromatic amines because the former have higher reactivities.^{1-4,7,8}

Aqueous PUs can be prepared by emulsification of hydrophobic PUs in water with the aid of emulsification agents and protective colloids. However, the emulsification with built-in hydrophilic groups result in better dispersing. This process does not require strong shear forces, yields finer particle size, gives better dispersing stability, and the product has reduced water sensitivity after evaporation of water. Building hydrophilic groups into the backbone means replacing other reactive ingredients (i.e., polyols, isocyanates) by special materials that contain ionic groups, ionic group precursors, or other water-soluble segments in their molecular structure. These units are called hydrophilic monomers or internal

emulsifiers. The sulfonate diamines and diols, or dihydroxy carboxylic acids, are the most important compounds.¹⁰ Among the dihydroxy carboxylic acids, DMPA has been frequently used as ionic building block.^{1-7,11} The advantage of using this compound is related to the steric hindrance of the COOH group so that its interaction with isocyanates is minimized.

Depending on the type of neutralization, PU dispersions can be cationic or anionic. Quaternization at the tertiary nitrogen atom yields cationic urethanes,¹²⁻¹⁴ whereas the neutralization of carboxylic acid groups gives anionic urethanes.^{1-3,5-8,11,15} The ionic centers are predominantly located on the surface of the dispersed particles, whereas the hydrophobic segments make the internal part of the particle. Another method worth mentioning for dispersion is the incorporation of polyoxyethylene segments into the backbone. This introduces water miscibility into the system but the resulting PU films remain water sensitive, and therefore it is not a desired method.¹⁰

The first step in the preparation of PUs is to synthesize isocyanate-terminated prepolymers. For this purpose, polyols are reacted with diisocyanates or with low molecular weight polyisocyanates. Some of the polyols are substituted with hydrophilic diols, which provide emulsification. The resulting polymer is then reacted with a neutralizing agent such as a triamine. The last step is chain extension with diamines. Reactions can be performed at a low temperature to minimize polyurea formation. A better technique than this direct reaction scheme is to block the isocyanate end groups before the dispersion step. This can be accomplished by mixing the prepolymer with a blocked amine or blocked hydrazine before dispersion. Ketimines or ketazimes, which are condensation products of amines and hydrazines with ketones can be used to block isocyanate groups. The blocked prepolymers are then mixed with diamines and made to be water borne. Chain extension occurs in each dispersed particle and high molecular weight builds up slowly. The blocked isocyanate groups are stable at ambient temperatures and deblock to create isocyanate groups at an elevated temperature. The isocyanate group then reacts with other reactive groups such as amine or hydroxyl groups to form the final PU. Most of the reactions are with amine groups because most of the water molecules will have left the medium at the elevated temperature of about 120°C.

To improve the film properties of the PU dispersion, some cosolvent such as *N*-methyl pyrrolidone, dimethyl formamide (DMF), and methyl ethyl ketone (MEK) can be used.³⁻⁷ These cosolvents have solvation property on both polar and nonpolar groups.¹⁶ Sometimes the use of a cosolvent remains as a necessity to achieve the necessary miscibility of raw materials.

EXPERIMENTAL

Materials and Methods

The experiments were performed in a four-neck lab scale glass reactor equipped with a mechanical stirrer, a thermometer, and an inlet and outlet for nitrogen gas. The reactions were performed under nitrogen atmosphere. The reactor was heated in an oil bath.

In the experiments, poly(propylene-ethylene) copolymer triol was used as polyol. Such polyols are readily available in the marketplace and are widely used in the PU industry, especially in PU foam production. Toluene diisocyanate (TDI) was used as diisocyanate. Two groups of experiments were performed, one with L-tartaric acid (TA) and the other with DMPA. Triethyl amine (TEA) was used as the neutralizing agent, and ethylene diamine was used as chain extender.

The polyol was dried at 120°C by passing dry nitrogen through it for 1 day. The cosolvents, DMF and MEK, and the blocking agent, methyl ethyl ketoxime (MEKO), were dried over molecular sieves.

TA was once used in the past, and its carboxyl groups had been neutralized before the polyaddition reaction. The researchers did not obtain satisfactory results.¹⁷ As a preliminary experiment, we repeated this, and neutralized carboxyl groups, as in the literature studies. It did not work and a gummy mass was formed within a few minutes. Therefore, TA was used without neutralization. Another preliminary experiment involved the chain extension step. Diethylene glycol was used as a linear difunctional polyol, but the reaction between carboxyl groups of TA and NCO groups of TDI was enhanced. Carbon dioxide evolution due to reaction between COOH and NCO was observed in the reactor, and a highly crosslinked material was formed. A third preliminary experiment involved the chain extension step. After the polyaddition reaction, the unblocked prepolymers were neutralized and cooled

Table I The Compositions of Formulations Used

Sample	Polyol (mol)	TDI (mol)	TA (mol)	DMPA (mol)	MEKO (mol)	TEA (mol)	Acetone (wt %)	EDA (mol)
T1 ^a	1.38	4	0.5	—	3	1.0	—	1.5
T2	1.17	4	0.8	—	3	1.6	—	1.5
T3	1.00	4	1.0	—	3	2.0	—	1.5
T4	0.76	4	1.4	—	3	2.8	5	1.5
D1	1.38	4	—	0.5	3	0.5	—	1.5
D2	1.17	4	—	0.8	3	0.8	—	1.5
D3	1.00	4	—	1.0	3	1.0	—	1.5
D4	0.76	4	—	1.4	3	1.4	5	1.5
D5	0.50	4	—	1.8	3	1.8	5	1.5

^a T, samples with TA; D, samples with DMPA.

down to 10°C to suppress the reaction of NCO-terminated prepolymers with water, and chain extension was affected with diamines that are reactive at this temperature. However, it was impossible to mix the very high viscosity prepolymer at this low temperature. Increasing the temperature resulted in chain extension with water and it yielded a gummy mass. A fourth preliminary experiment was performed at the dispersion step. After the deblocking reaction was completed, the neutralized prepolymers were homogeneously dispersed in water at 50°C, but tiny aggregates had formed during the heating period at 110°C. This aggregation may be attributed to the instability of prepolymer dispersions at high temperatures. After all of these preliminary trials, the following procedure was developed:

1. Polyol and hydrophilic monomer was dispersed in the cosolvent (50:50 w/w) and heated at 70°C under nitrogen atmosphere for 30 min to obtain a homogeneous mixture. This is important for the equal uniform distribution of hydrophilic monomer on the PU backbone. DMF was used with DMPA, and MEK was used with TA.
2. TDI was added with continuous stirring to the homogenized mixture, and the reaction was allowed to proceed for 3 h while using TA, and 4 h while using DMPA. The temperature was kept at 70°C. The reaction times were determined by the dibutyl amine back titration method.
3. After completion of the reaction, the prepolymer thus obtained was cooled to 50°C, and the free NCO groups were blocked with MEKO for about 2 h.
4. TEA was added to the mixture at 50°C to neutralize COOH groups of acids under continuous stirring for 30 min.
5. Water was added to the mixture and stirred to obtain dispersion of organic phase in water. The amount of water added was about 50% of total mass. In some formulations, the prepolymer had high viscosity, and acetone was added in these cases to obtain a good dispersion.

The formulations used in the experiments are described in Table I. In all samples, the NCO/OH molar ratio was taken to be 1.6. The percentage of acetone was based on total reaction mass.

Emulsification with Dimethylol Urea

T3 and D3 (see Table I) were selected to form a series of mixtures, because they did not need acetone in the process, and their films had high hardness. T3 and D3 can not be simply blended, because they yield granulation sometime after mixing. Methylol urea was used because of its compatibility with each type of resin. It was added to the mixture approximately up to the point in which successful blending occurred. The small aggregates that could not be dispersed by mixing and methylol urea addition were destroyed with acetone. The amount of methylol urea needed was between 22.9 and 26.7% of the total weight of the mixture, and it was constantly taken as 25% for the first set of experiments in which the mixture with maximum hardness was sought. The amount of acetone used was constant for the two sets of experiments, and it was 11.8% of the weight of the mixture. Table II shows the

Table II Compositions of Mixtures of D- and T-Type Resins with Methylol Urea

Sample	Mixture (wt %)	
	D3	T3
M1	100	0
M2	90	10
M3	80	20
M4	70	30
M5	60	40
M6	50	50
M7	40	60
M8	30	70
M9	0	100

compositions of the mixture mixed with methylol urea which is 25% overall.

To see the effect of the amount of methylol urea, the sample M5 was mixed with varying amounts of methylol urea, as seen in Table III.

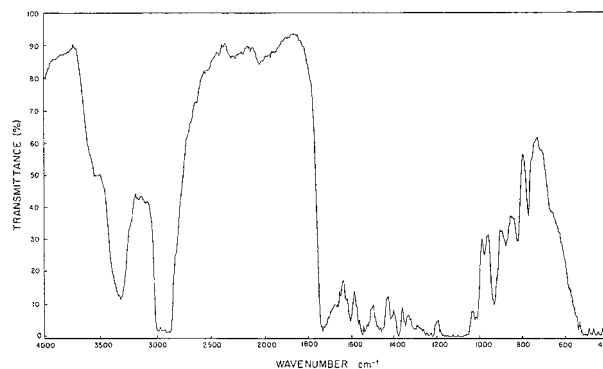
Determination of Properties

The particle size analysis was performed for water-borne resins. Other chemical, physical, and mechanical properties of resins were determined after applying each resin to a thickness of 50 μm and drying in an oven at 120°C. The following tests were used for evaluation:

1. Infrared (IR) spectrum. Samples studied were T3 and D3. Instrument: Hitachi, Model 270-30.
2. Particle size analysis. Instrument: Malvern Mastersizer, Version 1.2.
3. Hardness. Instrument: Braive Instruments, Model 3034; Persoz pendulum test was performed.

Table III Different Blends of M5 with Methylol Urea

Sample	Mixture (wt %)	
	M5	Methylol Urea
U1	75	25
U2	65	35
U3	50	50
U4	25	75
U5	0	100

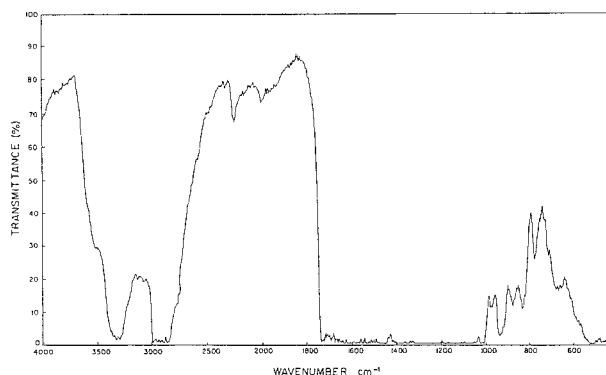
**Figure 1** IR spectrum of D3.

4. Adhesion. Tests were performed according to ASTM 3359-B.
5. Impact. Tests were performed according to ASTM D 2794. Instrument: Gardner impact tester, Model 5510.
6. Conical mandrel bending. Tests were performed according to ASTM D 522. Instrument: Braive Instruments, Model 1510.
7. Thermal gravimetric analysis. Instrument: Du Pont 9900.
8. Differential scanning calorimetry (DSC). Samples studied were T3 and D3. Instrument: Mettler TA 3000.

RESULTS AND DISCUSSION

IR Spectrum

The IR spectra of D3 and T3 are shown in Figures 1 and 2, respectively. All samples showed nearly the same spectrum. This is because the functional groups are similar in both cases, and the reactions are completed in all cases. The films are

**Figure 2** IR spectrum of T3.

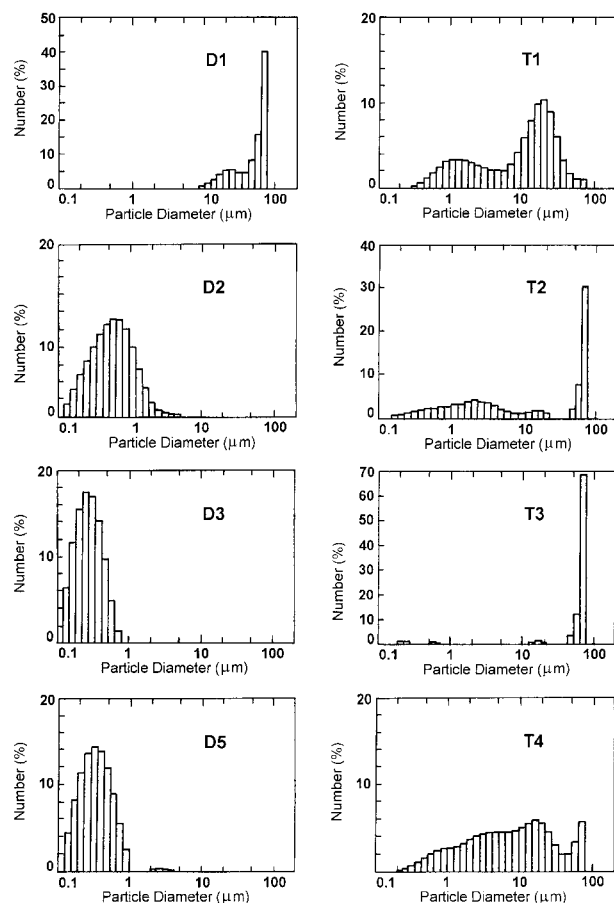


Figure 3 Particle size distributions in D- and T-type resins.

characterized by $2500\text{--}3500\text{ cm}^{-1}$ O—H stretching, 1740 cm^{-1} C—O stretching for carboxylic group, $675\text{--}900\text{ cm}^{-1}$ aromatic C—H bending, $1370\text{--}1470\text{ cm}^{-1}$ C—H bending for alkanes, and 3350 cm^{-1} N—H stretching for amides. The existence of N—H groups shows the formation of PU and/or polyurea bonds.

Stability

The stability of water-borne PU emulsions or dispersions is of primary importance for an industrial product. Gelation is usually expected if the stoichiometry is not properly adjusted, or if small ingredients induce some unusual reactions. The compositions given in Table I were checked for their shelf life at room temperature for a period of 2 months, and no gelation was observed in any case.

The particle size analyses discussed below were done by using the samples that were kept at room temperature for 2 months.

Particle Sizes

The particle size distributions of D- and T-type resins are given in Figure 3. Note that the polyol used here is a branched polymer, not linear. Therefore, the PU formed from it is also branched, and it forms particles in the micron range. Linear chain polymers form much smaller size.¹⁸ Samples D3, D4, and D5 showed very similar behavior, a Gaussian-like distribution, with particle sizes between 0.10 and $1\text{ }\mu\text{m}$. D2 is slightly asymmetric and the particle sizes extend to $10\text{ }\mu\text{m}$. In the case of D1, the particles had a slightly bimodal distribution and their sizes varied between 10 and $100\text{ }\mu\text{m}$. It is seen from Table I that D1 contains the highest amount of polyol. The decrease of polyol content decreases the size of resin particles in water as seen from D2 in Figure 3. Actually, as the polyol content decreases, DMPA content increases and thus the hydrophilicity of resin chains increases. This in turn results in the formation of particles with small sizes. However, further increase of DMPA beyond one mol does not change surface properties, and so the particle distribution keeps unchanged in D3 through D5.

The bimodal distribution in T1 is strongly seen in Figure 3. In T2, there appear two different distributions, and the particle sizes are shifted toward the large diameters as compared to T1. In T3, small size particles almost disappeared, and the particles are crowded around one large particle size. In T4, the particles have a nonuniform but continuous distribution, and smaller sizes are favored. The mean sizes of particles are given in Table IV.

In samples T1–T3, the mean particle size increases as the amount of TA increases. In water-dispersed resins made from linear polyols, it is known that the increase of ionic content on the

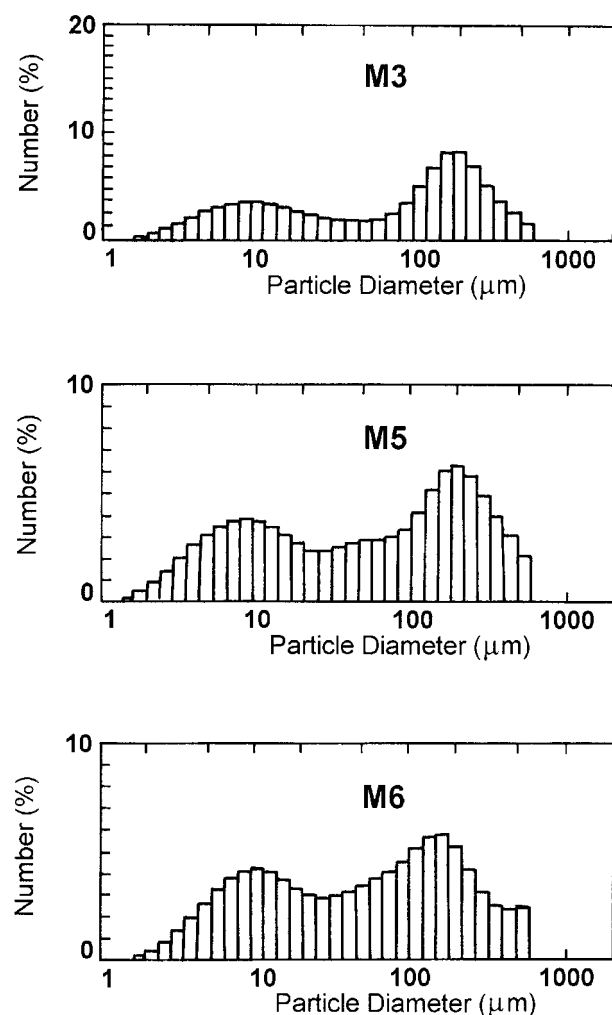
Table IV Mean Particle Sizes

Sample	Diameter (μm)
T1	14.79
T2	30.04
T3	59.60
T4	15.74
D1	49.57
D2	0.76
D3	0.31
D4	1.77
D5	0.47

Table V Mean Particle Sizes of Methylol Urea Containing Samples

Sample	Diameter (μm)
M3	127.07
M5	119.70
M6	106.49

resin molecule decreases the particle size. This is somehow true also when branched polyols and DMPA are used in the synthesis of resins, but it is not true when TA is used. As the frequency of occurrence of COOH on the backbone increases the probability of reaction with NCO, and thus the probability of extended branching increases. Branching increases the cohesion forces between chains, this in turn increases surface tension, and

**Figure 4** Particle size distribution in M-type resins.

thus increases particle sizes. This is what occurred in T1–T3. In T4, the amount of PO used decreased though the amount of TA increased. The decrease in PO naturally decreases the chance of propagation along the branches. Short branches do not contribute much to surface tension in the PU chains considered herein. The decrease of particle size with ionic content becomes significant after T3 in TA containing resins.

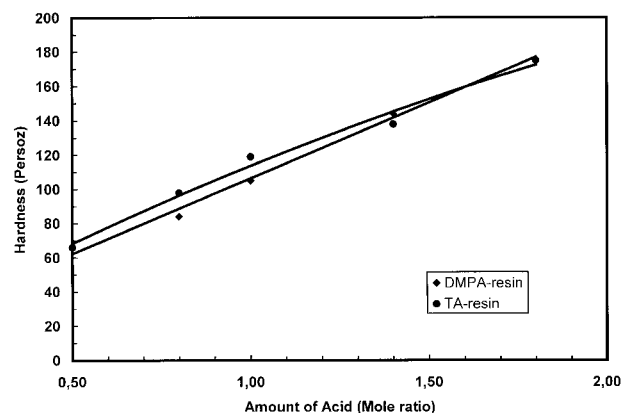
The average particle sizes of M3, M5, and M6 are given in Table V, and their particle size distributions are given in Figure 4.

It is seen from Figure 4 that they all exhibit bimodal distribution. The particle mean size decreases as TA-type resin increases in the mixture. This actually means an increase in the ionic content of the mixture. The mean particle sizes given in Table V are quite larger than those given in Table IV. This is because methylol urea causes crosslinking, and this naturally increases particle sizes.

Hardness

The change of hardness with respect to the amount of hydrophilic (i.e., acidic) monomer is shown in Figure 5. The increase of DMPA or TA in the polymer increases the hardness in either case. The effect of TA on the increase of hardness is little more than that of DMPA. Hardness seems to be more dependent on soft segments introduced by PO rather than on hard segments. That is, soft segments keep hardness low.

The incorporation of methylol urea into the network highly increases the hardness of samples. The hardness of D3 is 105 Persoz units, as seen from Figure 5, whereas the addition of methylol urea increases it to 148 Persoz units as seen from Figure 6 (i.e., see hardness of 0% TA). As the amount of TA containing resin is increased, the

**Figure 5** Change of hardness with the acid content.

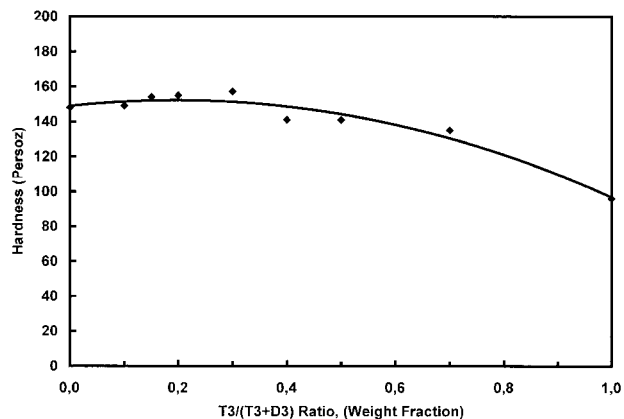


Figure 6 Hardness of M-type samples.

hardness slightly increases, passing through a maximum of 157 Persoz units, then it decreases especially after 70% TA-resin. Methylol urea has a negative effect on the hardness of T3. It decreases its hardness from 119 (see Fig. 5) to 96 Persoz units (see the last point in Fig. 6). This is an interesting result and needs further investigation. However, a possible explanation may be a possible wrinkling of the surface in the case of T3-methylol urea resin. Because the Persoz test counts the oscillations of a pendulum on the surface, the existence of small wrinkling may result in a false reading.

The sample that has the maximum hardness value (i.e., 157 Persoz) with a D3/T3 of 70:30, was modified further by increasing the methylol urea content. It is seen from Figure 7 that the increase in the urea content decreases the hardness. This may again be attributed to small wrinkling on the surface. Surface wrinkling is expected when very soft and very hard segments coexist. The increase in the methylol urea content in Figure 7, or TA based resin in Figure 6 results in wrinkling of the surface because both methylol urea and highly branched TA resins incorporate hard segments.

Other Properties

All samples had very good adhesion with a value of "5" in the ASTM 3359-B test. All samples resisted an impact energy of 2 J without any damage. Finally, they all passed the conical mandrel bending test, and no cracks were observed.

Thermal Gravimetric Analysis

Samples with TA started to dissociate at 210°C, whereas the ones with DMPA started at 227°C. Methylol urea lowers the dissociation tempera-

ture drastically to 165°C. Samples with TA were more heat resistant at higher temperatures than DMPA-based samples. About 83% of the initial matter of TA-based samples remained undissociated at 340°C, and in DMPA-based samples, the same amount remained undissociated at 292°C. In M7, 74% remained undecomposed at 326°C.

DSC

DSC curves of T3, D3, and M7 had a minimum at 420, 370, and 385°C, respectively. These are their decomposition temperatures. This also indicates that T-type samples are more resistant to thermal decomposition than D-type samples.

CONCLUSIONS

1. Poly (propylene-ethylene) copolymer and L-tartaric acid can be used in making water-borne resins.
2. The use of acids in high quantities improves some physical properties such as hardness, but acetone must be used in quantities of about 5% to lower viscosity and obtain good emulsification.
3. The particle size distributions of D2–D5 samples had simple Gaussian-like distributions between 0.10 and 1 μm . D1 and all T-type samples had bimodal or nonuniform distributions with particle sizes extending to 100 μm . Samples containing methylol urea exhibited bimodal distributions with much larger particle sizes.
4. Mean particle sizes increase with the increase of branching on the polymer backbone.

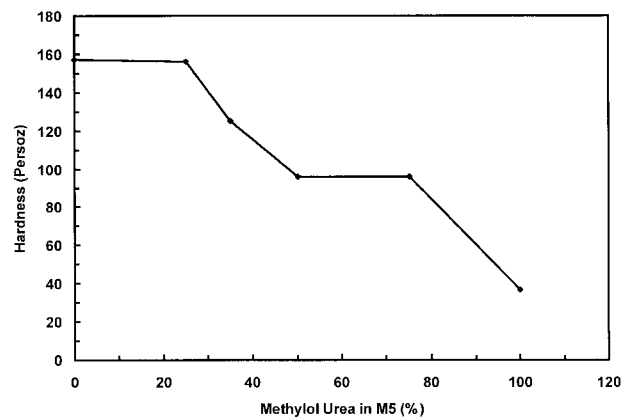


Figure 7 Change of hardness of M5 with methylol urea.

5. In both TA- and DMPA-based samples, hardness increases with the increase of the ionic character. This is because of higher molar ratios of organic acids. Hardness values in either type are close to each other, but TA-based resins have higher values. In methylol urea containing samples, hardness increases with the increase of the amount of TA-based resin up to 50%; after that, it shows a decrease. Hardness is not much affected by the type of organic acid, rather it is dependent on the weight fraction of soft chain polymer; the higher it is, the lower the hardness.
6. All samples have high adhesion and high impact resistance, and they all passed the mandrel bending test.
7. TA-based samples started to dissociate at 210°C and DMPA-based samples at 227°C. However, TA-based samples are more heat resistant than DMPA-based samples at higher temperatures.

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