

FATTY MONOMERS IN THERMOPLASTIC AND THERMOSETTING POLYMERS

By

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The Eastern Regional Research Center, U.S.D.A., has long been interested in the use of fatty derivatives in polymers or plastics, particularly because fats are renewable resources available in good supply at moderate price. They possess certain characteristics useful in the plastics field, such as long, flexible, lipophilic chains and ester and unsaturated centers available for introduction of additional functions.

Internal Plasticization

Considerable attention has been given to the use of fatty comonomers to plasticize addition polymers internally, that is by copolymerization. In vinyl plastics external plasticizers, such as monomeric esters, have given rise to certain ecological or health problems: the fogging of windshields and windows by plasticizer losses from the upholstery of new cars stored in the sun, the discharge of plasticizer mists from the stacks of processing factories, the extraction of plasticizers by blood administered from vinyl bags. In addition there is a gradual loss of external plasticizer with age. All these points provide arguments for permanent, internal plasticization.

Ideally, the efficiency of an internal plasticizer, or the degree to which it lowers the glass transition temperature of the base polymer, is greater the lower is its own glass temperature. Long polymethylenic side chains have been found to confer particularly low glass transition temperatures on homopolymers of which they are a part. Thus extrapolated plots of glass transition or flex temperature converge at -111° at a side-chain length of about C_{18} for several series of homopolymers: the n-alkyl acrylates, methacrylates, acrylamides, styrenes, the α -olefins and the vinyl fatty esters. In a simplified view, the lower the glass temperature of its homopolymer, the more a comonomer tends to lower the glass temperature of its copolymers.¹ In these terms comonomers with long fatty side chains should generally be efficient internal plasticizers.²

Side-Chain Crystallinity

On the other hand, polymers incorporating large amounts of comonomers with polymethylenic side chains often exhibit crystallinity not expected from the backbone structure. Several types of evidence show that much of this crystallinity is due to the long aliphatic side chains.^{3,4,5} As measured by differential scanning calorimetry poly(dodecyl acrylate) melted with a small endotherm, but poly(octadecyl acrylate) with a much larger absorption of heat; similarly the melting of poly(vinyl stearate) was much more sharply endothermic than that of vinyl laurate. The melting point of poly(N,n-octadecylacrylamide) or of poly(vinyl stearate) mixed with increasing amounts of poly(n-octadecyl acrylate) remained constant at about 55°. That of poly(dodecyl acrylate) increased linearly from about 12° to 55° as it was mixed with larger proportions of poly(octadecyl acrylate). Plots of heat of fusion ΔH_f vs. the number of methylene groups in the side chain were linear for poly(n-alkyl acrylates) and poly(vinyl esters). The heat of fusion was 777 cal/CH₂ group, or close to the 735 cal/CH₂ characteristic of the melting of n-alkanes. In these polymers a side-chain length of about 9 methylene groups was a minimum necessary for the appearance of crystallinity. In the stiffer poly(N,n-alkylacrylamides) the minimum was 12 methylene groups.

Properties of Co- and Terpolymers

Whether side-chain crystallinity is a problem in practice varies with the character of the short-side-chain, major monomer in a copolymer.⁶ Thus, in copolymers of methyl acrylate with octadecyl acrylate, heat of fusion becomes measurable once as much as 17% octadecyl acrylate is present. Thereafter heat of fusion, and therefore crystallinity, increases linearly as the weight per cent octadecyl acrylate increases. Polyacrylonitrile, however, is a stiff polymer. Copolymers rich in acrylonitrile appear to allow less conformational freedom to the backbone and therefore seem to delay and oppose the crystallization of fatty side chains. In copolymers of acrylonitrile and octadecyl acrylate, crystallization does not show up until 40% of the octadecyl acrylate is present. Glass transition temperature is lowered as a linear function of octadecyl acrylate content, until about 60% of octadecyl acrylate is present; to that composition the T_g (-111) of the hypothetical amorphous poly(octadecyl acrylate) remains effective in its effect of lowering glass transition temperature. Thereafter crystallinity obscures glass transition temperature as measured by differential scanning calorimetry. Copolymers of vinyl chloride with vinyl stearate display no heat of fusion until 40% of the latter is present and first show an apparent rise

in glass temperature at 45% vinyl stearate.

Table 1 lists physical property data on PVC plasticized with DOP, on poly (vinyl chloride-co-vinyl stearate), and on terpolymers of vinyl chloride with vinyl acetate and vinyl stearate.⁷ At equal proportions of plasticizing component, each copolymer had a little lower strength, higher modulus and lower elongation than its PVC-DOP counterpart, but several of the values were comparable. Flex temperatures T_f were not as low in the copolymers. The four terpolymer compositions showed improvements in elongation over copolymers of about the same strength. T_f was in some instances better, in others worse.

Polyblends

Vinyl polymers plasticized by copolymerization also suffer from a relatively short temperature range over which they have adequate strength. This problem together with others mentioned prompted investigation of polyblends of the vinyl copolymers with acrylonitrile-butadiene rubbers.⁸ The vinyl chloride copolymers studied contained 21, 36, and 47 wt % (or 5, 10 and 15 mole %) of vinyl stearate. Among the nitrile rubbers studied was the powdered rubber Hycar 1411* (0.336 mole fraction acrylonitrile, solubility to toluene extraction limited to ca. 11% by crosslinking). Physical properties of selected polyblends are gather in Table 2. In comparison with simple copolymers (Table 1), polyblends of poly (vinyl chloride-co-vinyl stearate) exhibited lower moduli and greater elongations in cases where ultimate strengths were about equal. These polyblends had good transparency and lost no weight by volatility. Improvement in toughness due to the polyblending was gauged by estimating the area under the stress-strain curves and comparing this area for polyblends to the area for the starting plastic. The polyblend of the vinyl polymer containing 21% vinyl stearate showed, at 25% NBR, 9 times the stress-strain area of the unblended copolymer. At 50% NBR this area ratio was 6.7. Thus, the polyblending greatly increased the total energy required to rupture these copolymers. Torsional moduli measured at 120° were over 250 psi, indicating worthwhile use-temperature ranges. PVC plasticized with DOP, which had very good viscoelastic properties unmodified, was benefited less by the polyblending. The stress-strain areas of its polyblends were only small, or fractional multiples of those of PVC-DOP alone. Its polyblends continued to show significant volatilization of DOP at high temperatures.

*Reference to a particular brand or firm name does not constitute an endorsement by the U. S. Department of Agriculture over similar products not mentioned.

Viscosity-Index Improvers

Long side-chain polymers also have merit in the lubricating field. Based on the literature and our preliminary studies, copolymers of long- and medium-side-chain acrylates or methacrylates are effective as viscosity-index improvers for base oils. At a given degree of polymerization, the effectiveness increases with the average length of the side chains.⁸

Urethane Foam Polyols

The use of tallow-based chemicals in some crosslinked, or thermosetting, polymers has also been under investigation. Recent emphasis has been on preparing fatty polyols for use in urethane foams, to whose cell walls polymethylene chains should contribute plasticity, low friability and resistance to humidity. At the beginning of this research, 9,10-dihydroxystearic acids were used as the source of the polyols. The threo and erythro dihydroxy acids are formed by the action of performic acid and permanganate, respectively, on oleic acid. Reaction with ethylene oxide in various molar ratios converted the dihydroxy acids to triols, the threo derivatives being of suitable fluidity as urethane polyols.⁹ Following a practice normal with castor oil, polyol equivalent weights were adjusted to 100 by enrichment with triisopropanolamine (TIPA). The isocyanates used were prepolymers resulting from action of excess toluene diisocyanate on sorbitol polyoxypropylate. Low-density rigid foams were made by mechanically stirring polyol and prepolymer with catalysts triethylenediamine and dibutyltin dilaurate, a silicone surfactant, and blowing agent fluorotrichloromethane. Densities and compressive strengths were comparable to those from conventional polyols. Other series of polyols were made by reaction of propylene oxide with the threo- and erythro-dihydroxystearic acids.^{10,11} Propylene oxide gave triols of suitable fluidity from both types of dihydroxy acid. Similarly, adjusted to equivalent weights of 100, these polyols foamed at lower, more convenient rates than the polyols made with ethylene oxide. The slower foaming resulted from the predominance of secondary rather than primary hydroxyl groups in the fatty ether esters.

Following the work with dihydroxystearic acids, a study of epoxidized glycerides as starting materials was undertaken. Liquid polyols were prepared from epoxidized glyceryl trioleate, glyceryl monooleate, lard oil, neatsfoot oil and soybean oil by hydration with 24% fluoboric acid.¹² Like the earlier polyols, these gave good low-density rigid foams by reaction with isocyanate prepolymers. They were also found to give satisfactory foams, in one-step systems, by reaction with a polymethylene polyphenylisocyanate.

Fire-retardance

A variation on this theme was the introduction of halogens for their fire-retardant action.¹³ Halogenated polyols were prepared from triolein, monoolein, lard and tallow both by treatment of the epoxidized glycerides with HX and by simple hypo-halogenation. With lard and tallow derivatives foam quality was improved by eliminating fully saturated, unoxygenated glycerides from the polyols by precipitation with acetone.¹⁴ In general, the best levels of fire retardance resulted from the use of small amounts of Sb_2O_3 in combination with the brominated polyols made from the epoxides.

Epoxidized Tallow-Trimethylolpropane Polyols

Although the acetone-precipitation step was effective in improving polyol quality, it was considered desirable, on cost considerations, to circumvent it. A way was sought to introduce hydroxyl groups by reactions attacking glyceride linkages at the same time as epoxide rings. It seemed feasible to alcoholize epoxidized tallow with polyhydric alcohols frequently used in urethane polyol synthesis. Trimethylolpropane (TMP) was found to lend itself readily to such reactions.^{15,16} Under appropriate conditions, alcoholysis was expected to occur at both oxirane and ester linkages. Each epoxy group would give rise, by reaction with TMP, to three hydroxyl groups. In addition, alcoholysis of glyceride linkages would confer hydroxyl functionality even on wholly saturated triglycerides. The reactions would give rise to a mixture of products including diglycerides, monoglycerides, fatty esters of TMP and TMP hydroxy ethers of the foregoing. With *p*-toluenesulfonic acid as catalyst (2%), investigation was made of the effect of reaction temperatures from 90 to 150° (by variation of refluxing solvent) and of the functional ratio of hydroxyl groups available from TMP to oxirane plus ester groups from epoxidized tallow. The best results were obtained at 120°. After 10 hours reaction unchanged TMP was extracted with water, and the polyols isolated as liquids of moderate viscosity. Table 3 (TA Series) relates the weight increases in formation of product, and the resulting hydroxyl numbers, to the functional ratios employed. Thin-layer chromatographic separations demonstrated the presence of components similar in polarity to those expected.

In order to introduce a fire-retardant aspect, similar reactions were carried out with a slow stream of hydrogen bromide as catalyst-reactant passing through the refluxing reaction mixture. These preparations are also summarized in Table 3 (TX Series); a functional ratio of 6.6 was used in each reaction. Reaction at 80° for 7 hours, with constant removal of water, gave the highest hydroxyl number and the lowest, but substantial bromide content.

The equivalent weights of both series of fat-based polyols were adjusted to 100 and 120 by incorporation of required amounts of TIPA or of NIAX LA-700 (an oxypropylated triamine). A typical foam formulation was: 17

Polyol TA 2	6.5 g
TIPA (to adjust OH equiv. to 120)	3.5 g
Dabco 33-LV	0.25 g
Silicone L 530	0.15 g
Fluorotrichloromethane	4.1 g
Polymethylene polyphenylisocyanate	12.3 g

Foam Properties

Test data on low-density rigid urethane foams made from polyols of the toluene-sulfonic acid series described are given in Table 4. Densities were between 1.6 and 2.0 lb/ft³, open cell contents all under 20% and compressive strengths all over 30 psi. Formulation at OH equivalents of 120 instead of 100 only slightly impaired foams involving TIPA as adjuvant and a little more those involving LA-700. The properties cited were all quite acceptable for low-density rigid foams.

Properties of the foams incorporating bromine are given in Table 5. Formulation at OH equivalents of 100 with TIPA gave low densities, open cell contents of about 20% and satisfactory compressive strengths. In a small-scale modification of ASTM Method D-1692 for relative flammability, each foam burned less than 20% of sample length. The foams from polyols at OH equivalents of 120 showed the same degree of flame resistance, but only the TX 3 polyol gave acceptable values of open cells and compressive strength.

Conclusions

The foregoing examples show that fat-based monomers have promise as building blocks of both uncrosslinked and cross-linked polymers. The growing shortages and higher prices of petroleum-based chemicals make exploitation of regularly renewable starting materials a particularly timely subject.

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Table 1. PVC Plasticized Externally and Internally

PVC, containing DOP, %:	36	42	47	
Tensile strength, psi	2526	1820	1326	
Modulus, psi	1400	700	500	
Elongation, %	130	234	219	
T_f, °C	-21	-40	-48	
Poly(Vinyl Chloride-co-Vinyl Stearate),				
Vinyl stearate, %	36	42	47	
Tensile strength, psi	2278	1692	1179	
Modulus, psi	2000	1200	800	
Elongation, %	117	168	155	
T_f, °C	-2	-19	-34	
VC-VA-VS, %^a:	60-5-35	52-14-34	40-27-33	38-24-39
Tensile strength, psi	2200	1930	1709	1310
Modulus, psi	1800	1300	600	400
Elongation, %	174	294	253	347
T_f, °C	-10	-11	-13	-20

^aTerpolymer of vinyl chloride, vinyl acetate, and vinyl stearate.

Table 2. Properties and Composition of Selected Polymers

Property	% NBR ^a Blended with VC-VS ₂₁ Copolymer ^b				% NBR ^a with PVC-DOP ₂₁ ^c	
	25	38	50	75	25	50
Strength, psi	2510	2380	1910	1640	3280	1850
Modulus, psi	1820	1200	719	415	1760	871
Elongation, %	278	399	356	600	290	238
T _f , °C	9	-9	-14	-22	-5	-19
Torsional Mod.						
23°C, psi	31,000	9000	1740	850	1120	770
120°C, psi	270	270	290	270	450	450
Transparency	v. clear	v. clear	v. clear	v. clear	clear	clear
Volatility	nil	nil	nil	nil	Significant	
Durometer A	99	93	79	69	95	85
Area, psi ^d	5031		3674		5706	2177
A _m /A _p ^e	9.13		6.67		1.61	0.61

^aHycar 1411. ^b Vinyl chloride-co-vinyl stearate (0.21 wt. fraction of vinyl stearate).

^cPoly(vinyl chloride) mixed with 0.21 wt. fraction di-2-ethylhexyl phthalate.

^dApproximate area under stress-strain curve. ^eRatio of stress-strain area of polyblend to that of plastic component.

Table 3. Polyols made by Reaction of Epoxidized Tallow with TMP

No.	OH ^a Ox + E	Reacn. Conditions		Wt. Increase, %	Hydroxyl Number	Br, %
		Temp., °C	Time, hr.			
Under catalysis by toluenesulfonic acid ^b						
TA 1	1.4	120	10	21	218	-
TA 2	2.1	120	10	28	257	-
TA 3	4.6	120	10	34	314	-
TA 4	6.6	120	10	44	340	-
Under catalysis and reaction with hydrogen bromide						
TX 1	6.6	110 ^c	12	130	105	42
TX 2	6.6	80 ^d	12	65	125	30
TX 3	6.6	80 ^{de}	7	75	231	25

^aFunctional ratio, or ratio of moles of OH from TMP to moles oxirane + ester from epoxidized tallow.

^bIn 60 ml toluene, 60 g epoxidized tallow (oxirane 3.0%, ester no. 188.8), 2% p-toluenesulfonic acid, TMP in accord with functional ratio OH/(Ox + E).

^cToluene solvent.

^dBenzene solvent.

^eWater continuously removed by Dean-Stark tube.

Table 4. Urethane Foam Properties - Toluenesulfonic Acid Series Polyols

Polyol	At OH Equivalent 100		Compressive Strength, psi	Density lb/ft ³	At OH Equivalent 120	
	Density lb/ft ³	Open Cells, %			Open Cells, %	Compressive Strength, psi
Equivalent wt. adjusted with TIPA						
TA 1	1.7	17	41			
TA 2	1.7	17	39	1.6	17	36
TA 3	1.6	16	38	1.6	19	34
TA 4	1.7	17	40	1.6	19	37
Equivalent wt. adjusted with NIAX LA 700						
TA 1	-	-	-	-	-	-
TA 2	1.8	14	49	1.7	19	36
TA 3	1.8	16	42	1.6	15	44
TA 4	2.0	15	60	-	16	35

Table 5. Urethane Foam Properties - HBR Series Polyols

Polyol	Density lb/ft ³	Open Cells, %	Compressive Strength, psi	Flammability % sample length
Adjusted with TIPA to OH equivalent of 100				
TX 1	1.6	21	34	< 20
TX 2	1.7	20	39	< 20
TX 3	1.8	20	36	< 20
Adjusted with TIPA to OH equivalent of 120				
TX 1	1.7	30-50	16	< 20
TX 2	1.8	38	29	< 20
TX 3	1.8	21	35	< 20