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PHENOXY RESINS CONTAINING PENDENT ETHYNYL GROUPS

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PREFACE

The research reported herein was performed as part of an effort directed towards the development of tougher/solvent resistant matrix resins for composites. Specifically this research was conducted to obtain fundamental information on how the properties of thermoplastics can be altered by crosslinking. This work was presented at the Southeast Regional Meeting of the American Chemical Society in Charlotte, North Carolina, November 1983.

INTRODUCTION

More extensive use of resin matrix/fiber reinforced composites in commercial aircraft has been identified as a viable means of reducing weight and thereby increasing fuel efficiency and payload. Although major improvements in composite properties (e.g. better damage tolerance and moisture resistance) have been made by improving the resin matrix (e.g. rubber or thermoplastic toughened epoxies and epoxy/bismaleimide blends), these resin systems still exhibit undesirable features such as limited prepreg shelflife, unforgiving and long cure cycles, and cocuring problems. Another approach to the development of better resin matrices involves the modification of thermoplastics. Commercial thermoplastics (e.g. Polysulfone, UDEL®) are excellent engineering materials with good toughness and thermoformability but poor solvent and creep resistance. Solvent and creep resistance are important requirements for composite structures on commercial airplanes which are designed for at least 50,000 hours of cumulative service at temperatures from -54 to 93°C in an environment which includes exposure to moisture and aircraft fluids (e.g. hydraulic fluid and paint stripper) while under load.

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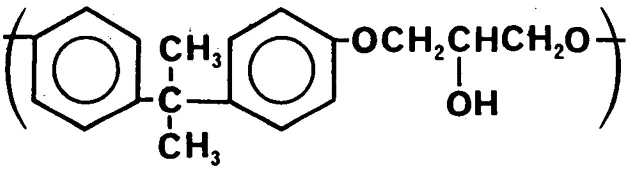
Research is underway to modify thermoplastics to improve the solvent resistance while retaining toughness and processability. Several routes are under investigation. One approach involves the use of reactive groups pendent along the backbone of the molecules. Upon exposure to heat, these pendent groups react to branch and crosslink the molecules. This report concerns preliminary research performed with phenoxy resins containing pendent ethynyl groups.

Phenoxy resins are relatively high molecular weight, amorphous engineering thermoplastics synthesized from the reaction of diphenols and epichlorohydrin using a strong base. PKHH, a phenoxy resin commercially available from Union Carbide Corporation, has the following chemical structure.



Linear phenoxy resins are reported to have good toughness, relatively high modulus, moderate thermal stability, excellent moldability, high abrasion resistance, and good adhesive strength (ref. 1,2). The major uses for phenoxy resins are as molding materials, coatings and adhesives. These thermoplastics are easily blow-molded and have been approved for use in food packaging. Furthermore, phenoxy resins have found use in the paint industry and are used as both automotive and marine finishes. Good adhesion is observed on metallic substrates such as copper, brass, galvanized steel, and aluminum, and on wood and many other non-metallic substances.

The chemical resistance of a phenoxy resin is dictated by the chemical structure and the amorphous nature of the polymer. It is resistant to acids and bases but soluble or swollen in polar solvents such as ketones, esters, and chlorinated hydrocarbons. To alleviate this problem and gain better weathering characteristics, several methods have been utilized to crosslink these resins. The pendent hydroxyl groups have been crosslinked by anhydrides, diisocyanates, urea- and melamine-formaldehyde resins (1). These methods usually employ two component systems and produce polymers that are unstable in solution.

The purpose of this investigation was to modify a phenoxy resin by incorporating a thermally reactive group pendent to the polymer chain. The resulting polymer could then be crosslinked when heated to produce a material with better solvent resistance and a higher softening temperature. This research was designed to provide fundamental information on the effect various amounts of pendent ethynyl groups had upon the processability of phenoxy resins and, when cured, upon the solvent resistance and glass transition temperature (Tg) or use temperature.

EXPERIMENTAL

Phenoxy Resin. - A commercial phenoxy resin, PKHH ($\overline{Mn} \approx 24{,}000$) was obtained from Union Carbide Corporation (3). Characterization is included in Tables 1 and 2, where PKHH is listed as polymer No. 1.

4-Ethynylbenzoyl Chloride. - Methyl-4-bromobenzoate was reacted with trimethylsilylacetylene using a palladium catalyst and the trimethylsilyl group was subsequently cleaved with potassium carbonate. After saponification, the carboxylic acid was converted to the acid chloride as previously reported (4). 4-Ethynylbenzoyl chloride was obtained as a yellow crystalline solid, m.p. 75-76°C, after recrystallization from hexane.

Phenoxy Resins with Pendent Groups. - Benzoyl chloride and/or 4-ethynylbenzoyl chloride was added to a solution of PKHH in methylene chloride (CH_2Cl_2) containing a small amount of triethylamine. After stirring overnight, the polymer was precipitated in methanol (MeOH), boiled in fresh MeOH, and dried in vacuo at 80°C to afford an off-white solid. Characterization of the various modified phenoxy resins is given in Tables 1 and 2 under the listings for polymers 2 through 7 as defined in Equation 1.

Ethynyl-Terminated Polysulfones (ETPS). - As previously reported (5), 4-ethynylbenzoyl chloride was reacted with a hydroxy-terminated polysulfone ($\overline{Mn}$ $\sim$8000) to form the ethnyl-terminated polysulfone (Tg of cured polymer by DSC = 198°C, η_{inh} = 0.34 dl/g, GPC peak retention time 18.35 min.).

Ethynyl-Terminated Polyester (ETPE). - As previously reported (4), 4-ethynylbenzoyl chloride was reacted with a hydroxy-terminated polyester ($\overline{Mn}$ $\sim$5000) to form the ethynyl-terminated polyester (Tg of cured polymer by DSC = 215°C, η_{inh} = 0.34 dl/g, GPC peak retention time 18.23 min.).

2,2-Bis(4-Ethynylbenzoyloxy-4'-phenyl)propane (BEBOP). - As previously reported (4), 4-ethynylbenzoyl chloride was reacted with 2,2-bis(4-hydroxyphenyl)propane to form 2,2-bis(4-ethynylbenzoyloxy-4'-phenyl)propane. Recrystallization from a mixture of ethanol and chloroform ($CHCl_3$) afforded pale yellow crystals, m.p. 182-183°C.

Blends. - Polymers and/or oligomers were dissolved in $CHCl_3$ and stirred to assure thorough mixing. The resulting blends were air-dried at ambient temperature for 18 hr and subsequently dried at 70°C for 4 hr.

Films. - Polymer solutions (20% w/v) in $CHCl_3$ were doctored onto plate glass, stage dried in a circulating air oven to a final temperature of 250°C and held for 0.5 hr at 250°C.

Characterization. - Inherent viscosity was obtained on 0.5% solutions in $CHCl_3$ at 25°C. Gel-permeation (size exclusion) chromatography was performed on a Waters Associates ALC/GPC 244 liquid chromatograph in $CHCl_3$ using μ-Styragel columns (10^6,10^5,10^4,10^3 A°), an ultraviolet detector (254 nm) and a flow rate of 2 ml/min. Differential scanning calorimetric (DSC) curves were obtained with a DuPont Model 990 Thermal Analyzer in combination with a standard DSC cell. Each sample was run in static air at a heating rate of 20°C/min with the apparent glass transition temperature (Tg) taken at the inflection point of the ΔT versus temperature curve. Torsional braid analyses (TBA) were conducted at a heating rate of 3°C/min in a nitrogen atmosphere over the temperature range of -100 to 300°C. Heat-up and cool-down curves were obtained on the same samples. Film solubilities were performed by soaking samples in $CHCl_3$ for 18 hr. Relative processability was studied by placing dried polymer between two pieces of Kapton (6) film, introducing into a preheated press, applying pressure and holding 10 min. Relative flow was rated by visual observation.

RESULTS AND DISCUSSION

As shown in equation (1), seven different phenoxy resins with various pendent groups were synthesized. The composition of the various polymers is shown in Table 1. Polymer 1 is PKHH, the commercial phenoxy resin. Polymer 2 contains 34% pendent ethynyl benzoyl groups and 66% residual hydroxy groups. The remaining polymers shown in Table 1 (polymers #3-7) have no residual hydroxy groups. Polymers 3, 4, 5, 6, and 7 contain 100%, 0%, 10%, 34%, and 66% 4-ethynylbenzoyloxy groups, respectively, while the remaining reactive sites were substituted with benzoyloxy groups. Inherent viscosity (η_{inh}), GPC and film flexibility data are provided in Table 1. Viscosities were as expected, with PKHH having the lowest value (0.40 dl/g) since no pendent hydroxy groups are substituted with larger groups. Polymer 2, which has 34% of the original hydroxy groups substituted, was slightly higher in viscosity than PKHH. The remaining polymers had similar viscosities, slightly higher than polymer 2, with polymer 3 having the highest viscosity at 0.52 dl/g. GPC peak retention times for all polymers except polymer 1 were very similar. Polymer 1 had the highest GPC peak retention time and, therefore, had the smallest average molecular size. These data were again predictable since this polymer has no substituent on the pendent hydroxy groups.

The last column in Table 1 concerns film flexibility. Cured films from polymers 1, 4, and 5 are fingernail creaseable and relatively tough. Cured films from polymers 2, 6, and 7 are flexible but not fingernail creaseable.

Polymer 3 formed a brittle film when cured to 250°C. This decrease in flexibility and toughness corresponds with an increasing amount of pendent ethynyl group substitution, indicating that the ethynyl groups reacted upon heating to provide polymers with increasing amounts of crosslinking.

Additional evidence for this interpretation is provided in Table 2. Both DSC and TBA data provide apparent Tgs. The first column under DSC data is the initial Tg, the second column is the exothermic peak temperature due to the reaction of the ethynyl groups and the third column provides the Tg after curing for 15 minutes at 300°C. Initial Tgs decreased slightly when the benzoyloxy group was substituted for the hydroxyl group and increased slightly when the 4-ethynylbenzoyloxy group was substituted for the hydroxyl group. No exothermic peaks were present for the polymers containing no ethynyl groups (numbers 1 and 4). For the polymers containing ethynyl groups, (numbers 2, 3, 5, 6, and 7) exothermic peak temperature decreased and the intensity increased as the ethynyl group content increased. The final Tgs correspond to the amount of ethynyl group present with higher Tgs for higher ethynyl content. Polymers without pendent ethynyl groups (numbers 1 and 4) displayed essentially no increase in the Tg after cure. TBA data is similar to DSC data, following the trend of higher Tg with increasing pendent ethynyl group content.

Cured films were tested for solubility in $CHCl_3$ and the resulting data are shown in the last column of Table 2. Polymers numbers 1 and 4 are uncrosslinked and soluble. At the other extreme, polymer number 3 is highly crosslinked and insoluble. The remaining polymer films swelled in $CHCl_3$ with increased swelling corresponding to decreased ethynyl content and crosslink density.

As shown in equation 2, four blends were prepared by blending polymer 6 (34% pendent ethynylbenzoyloxy substituted, 66% benzoyloxy substituted) with two polymers and one low molecular weight coreactant containing ethynyl groups. Polymer 8 was made by blending equal weights of polymer 6 and ETPS. Polymer 9 was made by blending equal weights of polymer number 6 and ETPE. Polymer 10 and 11 were made by blending polymer 6 with 10 and 30 weight percent of BEBOP, respectively. These compositions are listed in Table 3.

As indicated in Table 3, polymer 8 had an η_{inh} = 0.40, the approximate average of the two combined polymers (0.48 for #6, 0.34 for ETPS) while polymer 9 had η_{inh} = 0.57, which is higher, (for reasons not yet defined) than either of the starting materials (0.48 for #6, 0.34 for ETPE). GPC peak retention times are 18.37 and 17.50 for polymers 8 and 9, respectively. Polymers 8, 9, and 10 formed flexible films but the film from polymer 11 was brittle, due to higher crosslink density.

Table 4 gives thermal and solubility data for the cured blends. Initial and final polymer Tgs and exothermic peak by DSC are given. Polymer 8 had two distinct initial Tgs, corresponding approximately to those of each component, while the other blends displayed only one Tg initially. The exothermic peak was fairly low at 220°C (for polymer 8) and relatively high at 315°C for polymer 9. Polymers 10 and 11 displayed exothermic peaks at 283°C and 248°C, respectively, with the lower value corresponding to the blend with the highest ethynyl group content. Polymers 8 and 9 each displayed two Tgs after cure at values slightly above and slightly below those of cured polymer 6 and ETPS or ETPE, respectively. The presence of two Tgs indicates that the polymers are incompatible. The Tgs of polymers

10 and 11 after cure increased with increasing ethynyl group content. Data from TBA are very similar to that obtained by DSC.

The last column in Table 4 shows the effect of $CHCl_3$ on cured polymer films. Each of the four polymers was swollen in $CHCl_3$ but films made with BEBOP were affected less, indicating that they were more highly crosslinked than the ETPS and ETPE blends.

The processability of polymers 1-9 was compared by the simple method described in the experimental section. The press was preheated to 125°C, five polymers between films were inserted, a pressure of 100 lbs was applied and held for 10 min. Polymers (eg. polymers 1, 2 and 5) with good flow formed transparent disks. Polymers which did not exhibit good flow were opaque and still fibrous in nature (e.g. polymers 8 and 9). Other polymers flowed partially but still had some fibrous material present (polymers 4, 7, 6 and 3 in order of decreasing amount of flow). There is a trend in polymers 1-7, where increasing ethynyl content decreases polymer flow. The processability of polymer blends 8 and 9 was apparently controlled by the high Tg component, ETPS and ETPE, respectively.

CONCLUSIONS

A commercially available phenoxy resin (PKHH) was systematically modified by reacting with various amounts of 4-ethynylbenzoyl chloride and benzoyl chloride to provide a series of phenoxy resins containing different amounts of pendent ethynyl groups. This systematic change in ethynyl group content provided a corresponding change in polymer properties. As the ethynyl group content increased, film flexibility decreased, final Tg and solvent resistance increased. The modified resins, maintaining the excellent processability of PKHH, exhibited good flow under relatively mild conditions. Polymer blends were prepared by combining an ethynyl modified phenoxy resin with coreactants containing ethynyl groups. Several of the blends (8 and 9, Table 3) were incompatible and displayed two Tgs after curing. Blends prepared with a low molecular weight coreactant displayed decreased film flexibility, increased final Tg and solvent resistance with increased ethynyl group content. The crosslink density of these systems was systematically controlled by the incorporation of ethynyl groups.

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Table 1
Composition and Characterization of Polymers

Polymer No. (See Eq. 1)	Composition (See Eq. 1) where R =			η_{inh}, dl/g[1]	GPC Peak Retention Time, min[2]	Film Flexibility
	Mole % H	Mole % OC-C_6H_5	Mole % OC-C_6H_5-$C{\equiv}CH$			
1[3]	100	0	0	0.40	17.48[4]	Fingernail Creaseable
2	66	0	34	0.42	17.31	Flexible
3	0	0	100	0.52	17.34	Brittle
4	0	100	0	0.48	17.31	Fingernail Creaseable
5	0	90	10	0.46	17.33	Fingernail Creaseable
6	0	66	34	0.48	17.25	Flexible
7	0	34	66	0.47	17.30	Flexible

[1] Inherent viscosity of 0.5% solution in chloroform at 25°C

[2] Size exclusion chromatography using a bank of μ-Styragel columns (10^6, 10^5, 10^4, 10^3 Å) and chloroform as solvent

[3] Commercially available phenoxy resin from Union Carbide Corporation

[4] Number average molecular weight ~24,000 g/mole

Table 2
Thermal and Solubility Data of Polymer

Polymer (from Table 1)	DSC Data, °C[1]			TBA Data, °C[2]		Chloroform Solubility of Cured Resin[3]
	Initial Tg	Exothermic Peak	Final Tg[4]	Heatup Tg	Cooldown Tg	
1	100	none	101	99	101	Soluble
2	104	293	122	90	128	Moderate Swelling
3	102	257	ND[6]	92	235	Insoluble
4	87	none	88	82	87	Soluble
5	88	320	91	82	91	Pronounced Swelling
6	90	303	110	88	110	Moderate Swelling
7	95	277	144	89	150	Slight Swelling

[1] Differential scanning calorimetry at a heating rate of 20°C/min

[2] Torsional braid anaysis at a heating rate of 3°C/min

[3] Determined on thin films

[4] After curing for 15 min at 300°C in static air

[5] After heating to 300°C in nitrogen

[6] Not detected

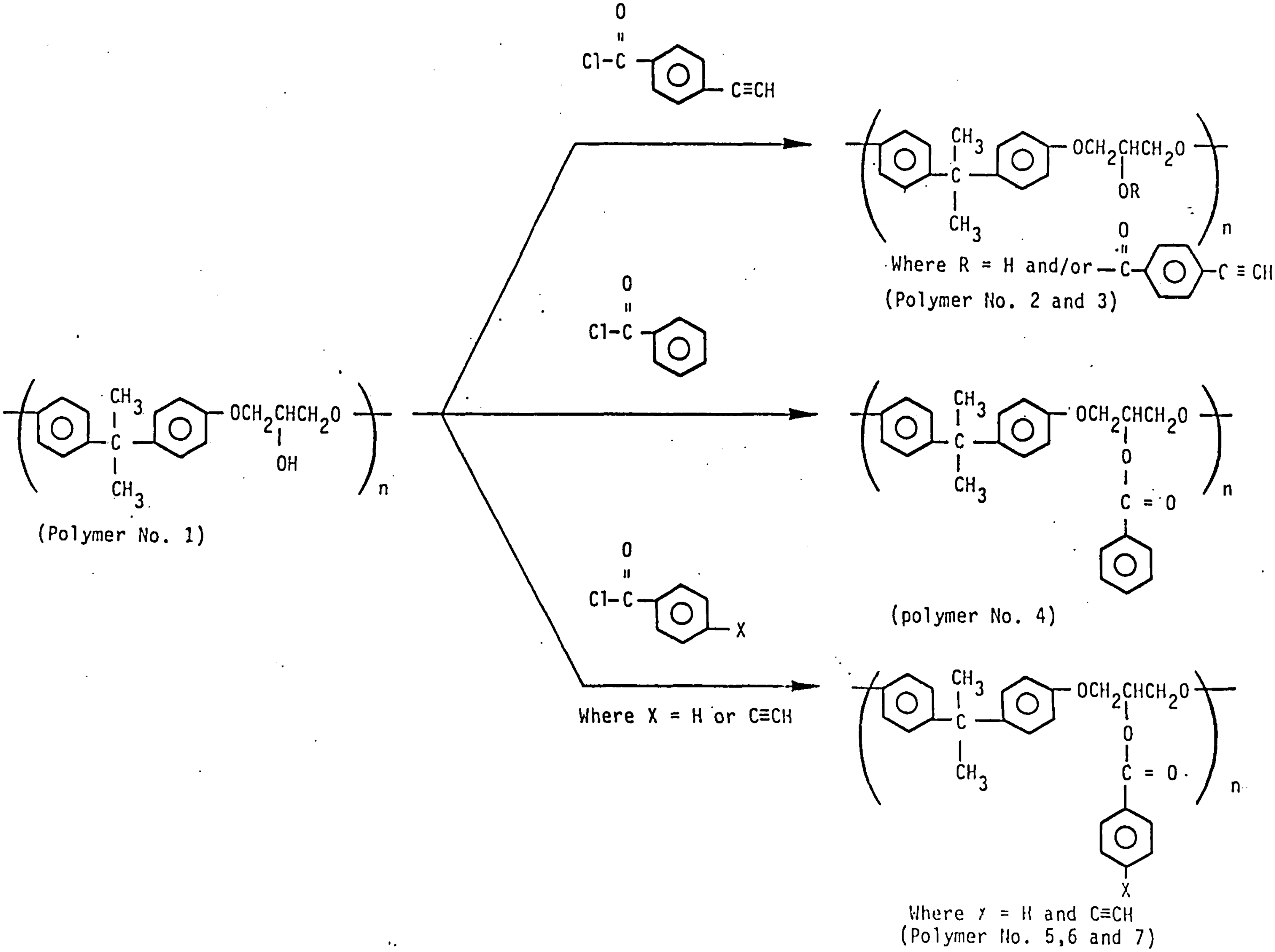
Table 3
Composition and Characterization of Blends

Polymer No.	Composition (See Eq. 2)	η_{inh}, dl/g	GPC Peak Retention Time, min	Film Flexibility
8	Polymer No. 6 + equal weight of ETPS	0.40	18.37	Flexible
9	Polymer No. 6 + equal weight of ETPE	0.57	17.58	Flexible
10	Polymer No. 6 + 10 weight % of BEBOP	—	—	Flexible
11	Polymer No. 6 + 30 weight % of BEBOP	—	—	Brittle

Table 4
Thermal and Solubility Data of Cured Blends

Polymer No. (from Table 3)	DSC Data, °C			TBA Data °C		Chloroform Solubility of Cured Resin
	Initial Tg	Exothermic Peak	Final Tg	Heatup Tg	Cooldown Tg	
8	98 and 155	220	112 and 185	91 and 187	113 and 197	Moderate Swelling
9	122	> 315	117 and 195	117	123 and 200	Moderate Swelling
10	96	283	117	85	114	Slight to Mod. Swelling
11	85	248	130	73	145	Slight Swelling

Equation 1
Preparation of Polymers



(Polymer No. 1)

Where R = H and/or $-C(=O)-C_6H_4-C\equiv CH$

(Polymer No. 2 and 3)

(polymer No. 4)

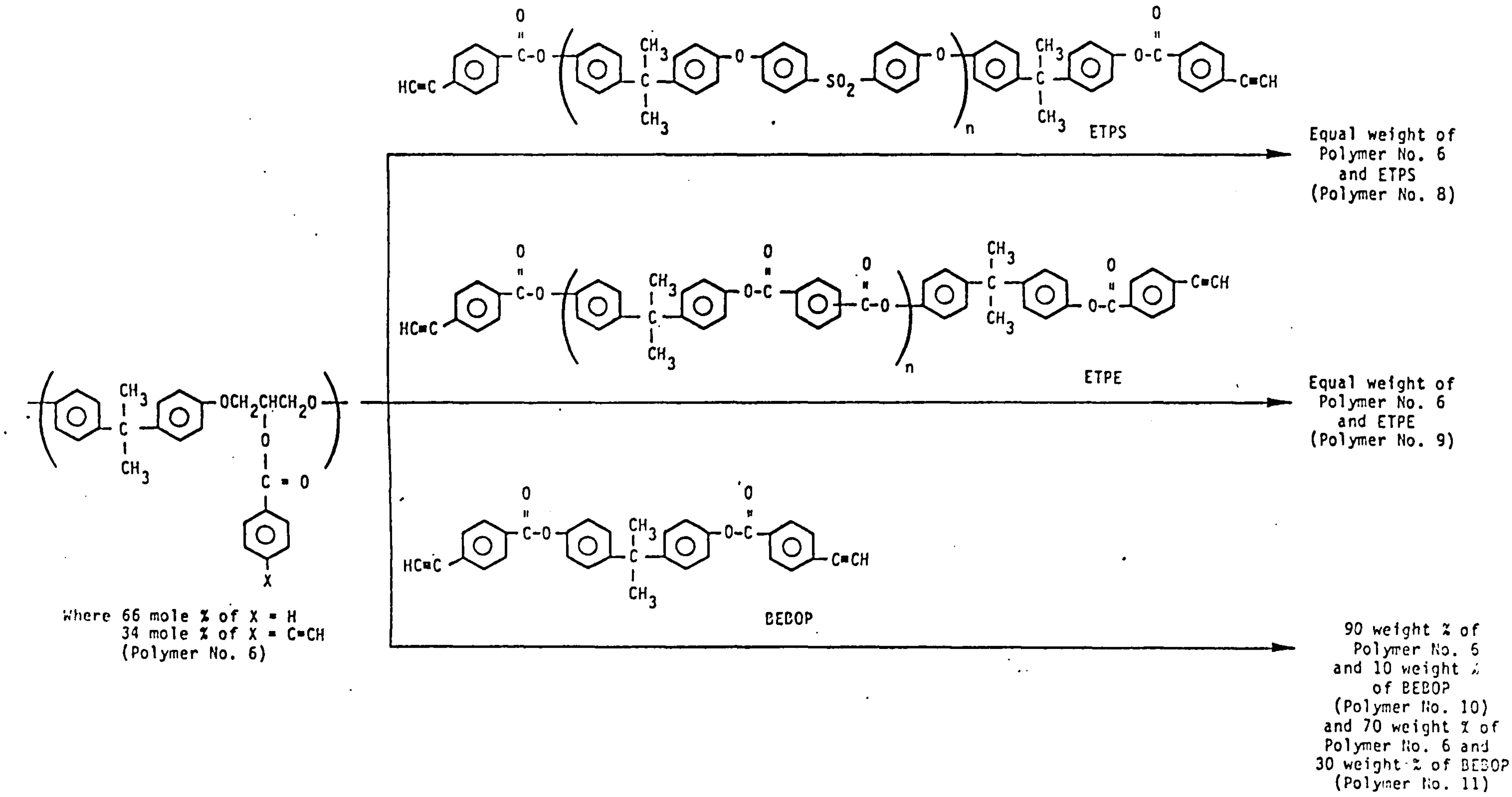
Where X = H or C≡CH

Where X = H and C≡CH

(Polymer No. 5,6 and 7)

Equation 2

Preparation of Blends



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16. Abstract

As part of an effort on tougher/solvent resistant matrix resins for composites, research has been directed towards exploring methods to improve the solvent resistance of linear amorphous thermoplastics. Ethynyl reactive groups have been placed on the ends of oligomers and pendent along the polymer chain and subsequently thermally reacted to provide crosslinking and thus improvement in solvent resistance. This concept has now been extended to another thermoplastic, a phenoxy resin. A commercially available phenoxy resin (PKHH) was systematically modified by reaction of the pendent hydroxyl groups on the phenoxy resin with various amounts of 4-ethynylbenzoyl chloride. As the pendent ethynyl group content in the phenoxy resin increased, the cured resin exhibited a higher glass transition temperature, better solvent resistance and less flexibility. The solvent resistance was further improved by coreacting a low molecular weight diethynyl compound, 2,2-bis(4-ethynylbenzoyloxy-4'-phenyl)propane, with a phenoxy resin containing pendent ethynyl groups.

17. Key Words (Suggested by Author(s))

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