Water Vapor Transmission Reduction in CARILON® Polymer Blends with Novolac Resin

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P. A. Westbrook, J. M. Machado

Technical Progress Report **WRC 26-92**
Project No. 62182

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Water Vapor Transmission Reduction in CARILON® Polymer Blends with Novolac Resin

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Project No. 62182
CARILON Barrier Packaging

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ABSTRACT

This work demonstrates a threefold decrease in water vapor transport rate for miscible blends of CARILON® Polymer and up to 15 percent by weight novolac resin relative to unmodified polyketone. Water absorption experiments show that the unmodified material exhibits nonequilibrium swelling and therefore plasticization by water. Water desorption experiments show that addition of novolac significantly reduces the diffusion coefficient of water and has a weak effect on water solubility in polyketone. As a result, the permeability of water in the blends is also reduced. All materials exhibit a non-Fickian diffusion behavior whereby the diffusion coefficient is proportional to the water concentration. Other properties such as strength, stiffness and impact resistance at ambient temperature are maintained in the blends; however, extraction of the rather low molecular weight novolac resin remains a problem.

Technical Progress Report **WRC 26-92**

WATER VAPOR TRANSMISSION REDUCTION IN CARILON® POLYMER BLENDS WITH NOVOLAC RESIN

by

P. A. Westbrook
J. M. Machado

INTRODUCTION

Owing to its engineering thermoplastic properties and relatively low cost, CARILON® Polymer is being developed as a replacement material for glass in retortable food packaging (1). The high melting point (220°C for CARILON EP) and good mechanical properties of CARILON Polymer allow sealed containers to survive food sterilization (via heat and pressure) without collapsing (panelling). Foods such as fruits and vegetables must be packaged in this way; packaged meals such as spaghetti, baby food, etc. are also subjected to retort. The retortable food packaging market is therefore quite large and there is a considerable cost incentive for replacement of glass.

To penetrate this market, our business has targeted individual serving containers of the "Lunch Bucket" type which may contain spaghetti or other foods. Typically these are eight fluid ounce containers. The prototype CARILON polymer package has a thin wall (target of 0.020 inch) with a metallic lid. Taste testing of prototype containers has been performed in conjunction with Heinz (2,3).

A major technical problem associated with CARILON Polymer in this application is its intrinsically high water permeability. The permeability of oxygen and other gases is low enough for this application (1). The diffusion coefficient and solubility of water in CARILON EP is approximately 120 mil^2/day and two to three percent, respectively. These values can change somewhat from lot to lot depending on the percent crystallinity and/or other morphological factors. The resulting water loss from a 27 mil wall, 28 in^2 cup molded from neat CARILON Polymer can be 10 percent per year or higher. Such high water loss rates will alter the taste of packaged foods and cause them to discolor over a period of time. The business objective for water permeation rate is three percent per year or less from such containers. Any such modification to the polymer or container to achieve this goal should not add more than one cent to the cost of the cup, presently estimated to be seven cents, and should not affect the ability of the material to survive retort, transportation, etc.

Several methods of reducing water permeability in CARILON Polymer cups have already been demonstrated. The use of a thin, outer coating of Saran (PVDC) reduces the water permeability to one percent per year or less (4,5). Cups utilizing this technology have passed taste tests performed by Heinz (2,3). The use of a polypropylene inner liner can reduce water permeability to one percent per year. Cups molded from a ternary blend of CARILON EP, polypropylene and a compatibilizer, maleated KRATON® rubber, have demonstrated three percent per year water permeability (5,6,7). Overwraps, such as an adhesive label or shrink-wrap for bulk packaging also reduce permeability substantially (8). These technologies meet the permeability and cost objectives but other issues such as FDA status or recyclability may become an issue for some of these approaches. As a result these techniques may become useful for some applications such as non-food packaging, etc.

It is therefore desirable to develop a homogeneous monolayer cup from a blend of CARILON Polymer and another material(s). Such a blend should possess significantly lower water permeability while maintaining a proper balance of other properties, including FDA status, after-use issues, etc. Such a blend would require only a single processing step and the resulting mechanical and water transport properties may not be as sensitive (as inhomogeneous blends) to processing variations. The present work is therefore focussed on reduction of the Water Vapor Transport Rate (WVTR) in CARILON Polymer via formation of miscible blends.

BACKGROUND

Miscible Blends of CARILON Polymer

Strong dipole-dipole interaction and/or hydrogen bonding between polymers can drive thermodynamic miscibility. To achieve miscibility, the functional interaction must be of sufficient strength and concentration to overcome the unfavorable dispersive effects of polymer mixing. Since the ketone group in CARILON Polymer is moderately polar and highly prevalent, polyketone seems to possess favorable characteristics for the formation of miscible blends with other materials.

In recent studies, it has been shown that polyketone is an effective hydrogen bond acceptor. Miscible blends have been prepared with polymers which have sufficiently acidic protons such as polyvinyl phenol, styrene-vinyl phenol copolymers, and novolacs based upon phenol, m-cresol and resorcinol (9-13). Interestingly, the hydrogens of aliphatic polyols, such as polyvinyl alcohol and ethylene vinyl alcohol, are not sufficiently acidic to form miscible blends with polyketone and WVTR is not improved (14). This apparently anamolous behavior may reflect a high level of self-association which must be overcome in aliphatic alcolols. Miscible blends of polyketone have also been prepared with polymers which have a strong dipole moment such as polyacrylonitrile and styrene-acrylonitrile copolymer (10,11,13).

This propensity for hydrogen bonding also makes CARILON Polymer a poor water barrier. The solubility of water in CARILON Polymer is quite high, two to three percent at room temperature. Once swelled, the diffusivity of water through CARILON Polymer is also high, approximately 120 mils^2/day (or greater). Also contributing to high WVTR is the relatively low crystallinity of CARILON EP, approximately 30 percent.

The present work investigates the use of miscible blends to reduce the WVTR in CARILON Polymer. Blends of CARILON Polymer with phenol-based novolacs are of specific interest. Preliminary results using these systems have shown that alkyl substituted phenol-based novolacs are not as effective at reducing WVTR as unsubstituted phenol-based novolacs (15). Novolacs are oligomeric materials (typically 10,000 molecular weight) produced from the acid catalyzed reaction of formaldehyde with an excess of phenol or substituted phenol. The structure of the novolac resin is often branched and irregular but is commonly thought of as phenol groups linked in the ortho positions by methylene groups. These low molecular weight polymers are typically molded in the presence of a cross-linking agent, such as hexamethylenediamine, to produce a cured phenolic network with high cross-link density. Such thermosets are known for good thermal and dimensional stability and low cost. Certain cured novolac resin systems have FDA approval and they may find application as aluminum can liners.

Polyvinylphenol can be polymerized by free radical polymerization. This material was obtained from Hoechst-Celanese and can be used for curing thermoset resins. Our interest in polyvinylphenol is derived from its comparatively higher molecular weight relative to the novolac resins. Increased molecular weight should enhance several desirable attributes of the blend such as better toughness, fewer water extractables, etc.

For this investigation, CARILON Polymer and the resins are blended together and the novolac remains uncured in the blend. The phase behavior of this system has been reported previously (9). By analysis of the melting point depression behavior in blends as a function of novolac concentration, the interaction parameter, χ, was determined to be negative and on the order of unity. This large value for χ indicates that the thermodynamic driving force for miscibility is quite strong and, indeed, unsubstituted novolacs were found to be miscible with CARILON Polymer over the entire composition range.

Since the novolac resin hydrogen-bonds with CARILON Polymer strongly enough to drive miscibility, perhaps the propensity of the blend to hydrogen-bond with water will be reduced. Further, incorporation of meta-linked aromatic groups into the amorphous phase of polyketone may reduce the mobility of diffusing gases. Thus, the solubility, diffusivity and therefore the permeability of water may subsequently be reduced in the miscible blend.

Determination of Permeability, Solubility and Diffusivity

The permeability (P), solubility (S) and diffusivity (D) of water in materials are related through the following well known equation:

$$P = S \times D \qquad (1)$$

The permeability of water through CARILON Polymer can be determined directly by measuring the rate of weight loss as a function of time using sealed cups. This technique allows one to directly measure the effects of retort.

One can independently determine the solubility and diffusivity of water in CARILON Polymer from absorption (weight gain) studies. By assuming diffusion into an infinite slab from two surfaces, the unsteady Fickian diffusion equation can be solved explicitly (15). The solution is an infinite series and, retaining only the first term, can be expressed as follows (15):

$$\frac{Q_t - Q_i}{Q_{eq} - Q_i} = \frac{8}{\Pi^2} \exp\left[-\frac{\Pi^2 D}{L^2} t\right] + \ldots \qquad (2)$$

where Q_i is the initial concentration, Q_{eq} is the equilibrium concentration (solubility), and Q_t is the concentration of water at any time, "t." "D" is the diffusion coefficient and L is the thickness of the slab. One can plot the logarithm of the absorption coefficient versus time to obtain the diffusion coefficient (D). The solubility (S) is determined simply from the equilibrium weight gain.

EXPERIMENTAL

The polymeric materials used in this investigation are summarized in Table 1. The CARILON Polymers are ethylene-propylene-carbon monoxide terpolymers of low LVN to facilitate thin wall injection molding. The novolacs are unsubstituted phenol-based materials of two molecular weights. Several blends ranging in novolac content up to 15 percent by weight were made. The blends were melt compounded on a 30mm Haake co-rotating twin screw extruder operating at 200 RPM and about 250°C with a relatively mild screw configuration. Seven ounce cups were molded on an Arburg Alrounder injection molding machine. Wall thickness of the cups was 0.027 inch.

Permeability before and after retort was determined by measuring weight loss as a function of time from sealed cups filled with water. Diffusivity and solubility measurements were obtained from weight gain measurements on immersion coupons. Strength of blends was determined in tension and flexure while stiffness of blends as a function of temperature was determined by a rheovibron operating at one Hertz. Thermal properties such as glass transition temperature and melting temperature were obtained by differential scanning calorimetry.

The relative toughness of CARILON Polymer and blends containing novolac resin was determined by impact testing of cups. An instrumented Dynatup impact machine was used with a weight of 6.23 pounds falling from a height of three feet. The tup diameter is 0.5 inch and it impacted the bottom of the cup.

RESULTS AND DISCUSSION

Processing of Blends

Blends of CARILON Polymer and novolac resin melt-processed well with no obvious signs of chemical degradation or cross-linking. The use of low molecular weight novolac resins may actually improve processability as they may act as melt plasticizers. The novolac resin itself has a yellow color which translates itself into the cup. The surfaces of the cups made from blends have a higher gloss finish relative to the neat CARILON Polymer.

One potential problem is the rather strong odor of novolac resin encountered during molding. Also, after retort, the cups made from blends have a certain waxy feel. These effects are probably a result of the low molecular weight of the novolac resin. Increasing the molecular weight from 10,000 (HRJ-2190) to 25,000 (GP-2074, not commercially available) only modestly improved these aspects. If interest continues in novolac blends, we anticipate FDA issues which will have to be resolved at a later date.

WVTR Reduction in Blends

Permeability of water through injection molded cups was measured directly by weight loss measurements. The slope of the weight loss curve in the steady state region is proportional to the permeability. Figure 1 shows, for example, that the novolac modified (10 percent by weight) CARILON Polymer exhibits water permeability (slope) approximately three times less than that of the neat material. Also shown in Figure 1 is an increased induction time for water permeation. This induction time is theoretically proportional to the diffusivity but calculation of the diffusion coefficient by this method is not generally deemed practical. However, an apparent reduction of water diffusivity by a factor of three to five is indicated from this data.

The reduction of water permeability for three CARILON EP materials blended with two phenol-based novolac resins is demonstrated in Figure 2 as a function of novolac content. Water permeability in molded cups is observed to drop sharply with novolac content. Water loss of three percent per year after retort is demonstrated for all three CARILON Polymers. Depending on the CARILON Polymer lot, it requires 10 to 15 percent by weight novolac resin to achieve acceptable WVTR. The observed variation in WVTR reduction is likely a result of morphological differences between polyketones such as degree of crystallinity as well as differences in molding conditions, etc. There seems to be more variability in WVTR among polyketones than between novolacs.

The water permeability data obtained for blends of CARILON EP and polyvinylphenol appear in Figure 3 as a function of polyvinylphenol content. Water permeability is observed to drop with polyvinylphenol content but the effect is not nearly as strong as was observed for the novolac materials. As a result, these blends will not be considered further in this report.

Water Absorption Studies

In order to gain a better understanding of the mechanisms of WVTR reduction in blends of CARILON Polymer and novolac resin, water absorption and desorption studies were performed on thin films cut from molded cups (0.027 inch thick).

Figure 4a shows water absorption data at room temperature for neat CARILON Polymer and blends with novolac resins. The water absorption behavior of the neat CARILON Polymer is different from that of the blends. Equilibrium water absorption is not observed even after 4000 hours exposure of these thin samples. Indeed there appears to be two modes of absorption. The unmodified material absorbs approximately two percent by weight of water in the first few days. Then a slow process of swelling and further absorption and plasticization begins. This secondary absorption seems to be nearly linear with time and therefore is non-Fickian.

The blends also absorb nearly two percent (by weight) water and then reach a pseudo-equilibrium within one week. Actually the weight seems to decrease for the more concentrated novolac blends and this weight loss can be attributed to extraction of the low molecular weight novolac material. To illustrate this, the blend materials were dried and a net weight loss of nearly one percent was observed after 2000 hours of immersion (within our experimental error, no extraction was observed for neat polyketone after 4000 hours immersion). The samples were then reimmersed in water. Figure 4b shows that the second set of weight gain data quickly approaches the long-term weight gain values from the first absorption experiment, then further extraction and weight loss continues.

In light of the extraction process occurring during the absorption experiment, it is invalid to determine diffusion parameters from these data. Rather, desorption kinetics are used. Figure 5 shows water desorption from saturated coupons in a zero humidity environment for comparison to the absorption data. One observes that water desorption occurs at a faster rate and to a greater extent than absorption. The latter is due to leaching of low molecular weight materials in the absorption experiment. Finally, the samples were dried in a vacuum oven to determine the total sorbed water for these experiments.

The unsteady diffusion data from the first few days of desorption are plotted according to Equation 2 in order to determine the diffusion coefficient. From the nonlinear desorption behavior observed in Figure 6, it is shown that desorption is a non-Fickian process, especially for the blends. That is, the diffusion coefficient is proportional to the water content as well as the novolac concentration. However, the initial slope of these four curves is interpreted as proportional to the diffusion coefficient of water in the saturated material. These values are probably most important because they may be more indicative of the actual diffusion coefficient in polyketone, which is highly plasticized with water.

Table 2 summarizes diffusion parameters for water in CARILON Polymer and blends with novolac resin. The solubility of water is a weak function of novolac content while the diffusion coefficient decreases substantially. These observations are supported by independently determined diffusivity numbers from permeability experiments (described earlier). Therefore the observed three-fold drop of permeability in the blends can be accounted for via similar reductions of the diffusivity.

Thermal-Mechanical Properties of Blends

As indicated above, the balance of properties in the blends is also of interest. Figure 7 shows the dynamic mechanical storage modulus as a function of novolac content. At ambient temperature, the stiffness of the blend increases sharply as the novolac content approaches 20 percent. This is primarily a result of increases in the glass transition temperature from just below ambient in the neat material to over 40 °C in the 20 percent novolac blend (see also Figure 8). Above the glass transition temperature, Figure 7 shows the stiffness of the blends decreases with novolac concentration. This is because the overall crystallinity of the blend is decreasing. As a result, it may be desirable to minimize the novolac content from the standpoint of surviving the retort cycle. Figure 8 shows the glass transition temperature of the blends as a function of total polyketone content for the novolac blends. There is good agreement between DSC and DMA methods. The observed deviation from Fox-Flory behavior is attributable to the strong hydrogen-bonding in the miscible blend. Of course, as the material absorbs water, the glass transition temperature will drop sharply due to plasticization. Figure 9 shows the ambient temperature strength of the blends may increase somewhat with novolac content up to 30 percent.

Impact properties of the molded cups are summarized in Table 3. It is observed that with low molecular weight constituents (90064/HRJ-2190) toughness drops off sharply with novolac concentration. This may be a result of the brittle-ductile transition for low molecular weight materials and the use of a low LVN CARILON EP. As the molecular weight of the constituents is increased, (91026/GP-2074) toughness of the blends does not decrease relative to the neat material. Therefore it seems that an LVN of at least 1.3 is required for blending with novolac resins.

CONCLUSIONS

This investigation of miscible blends of novolac resins and CARILON Polymer has shown that addition of up to 15 percent by weight novolac resin can reduce the WVTR of CARILON EP by a factor of three. This reduction of water permeability can be accounted for by a similar reduction of the diffusivity of water in CARILON Polymer; water solubility in polyketone- novolac blends is only weakly affected. This reduction in diffusion coefficient is sufficient to achieve the objective of three percent per year water permeability in eight ounce cups. The balance of properties of polyketone-novolac blends seems to be maintained.

One disadvantage for the use of low molecular weight amorphous novolac resins to reduce WVTR in polyketone blends is the inherent mobility of the additive. This will lead to extraction problems and may preclude FDA approval. If interest in novolac blends continues, we recommend cleaning the novolac before compounding with CARILON polymer by removing the low molecular weight residual monomers and oligomers via extraction in hot water.

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Table 1 Materials used in this study

Polymer Designation	Description
90064	CARILON EP R-1000 Polymer, 222 C melting point, 1.05 LVN.
91026	CARILON EP R-1000 Polymer, 222 C melting point, 1.37 LVN.
91032	CARILON EP R-1000 Polymer, 226 C melting point, 1.30 LVN.
HRJ-2190	Phenol-Formaldehyde novolac resin, manufactured by Schenectady Chemical Co., 110 C melting point, 10,000 molecular weight.
GP-2070	Phenol-Formaldehyde novolac resin, manufactured by Georgia-Pacific, 110 C melting point, 25,000 molecular weight.
PVPh	Polyvinylphenol resin, manufactured by Hoescht-Celanese, 50,000 molecular weight.

Table 2 A summary of diffusion parameters of polyketone-novolac blends as determined by water desorption and permeability experiments.

MATERIAL COMPOSITION	S(desorb) (percent)	D(desorb) (mil^2/day)	D(wt loss) (mil^2/day)	P(wt loss) (gm*mil/100in^2/day)
CARILON 91032	2.40	114		
CARILON 90064			133	5.82
032+ 5%GP2076	2.23	36		
032+10%GP2076	2.46	33		
064+10%HRJ2190			24	2.17
032+15%GP2076	2.61	29		

Table 3 Impact resistance of cups made from blends of CARILON polymer and novolac resins.

Specimen	Maximum Load (lbs)	Energy (ft-lbs)	Specimen	Maximum Load (lbs)	Energy (ft-lbs)
CONTROL	105	1.81	CONTROL	90.0	1.32
90/064			91/026		
1.1 LVN			1.38 LVN		
1% HRJ-2190	93.8	1.44			
2% HRJ-2190	83.4	1.01			
5% HRJ-2190	94.4	1.49			
10%HRJ-2190	74.2	0.83	10%HRJ-2190	112	1.42
			5% GP-2074	103	1.35
			10% GP-2074	124	1.65
			15% GP-2074	137	1.85

Figure 1 Weight loss from water filled cups as a function of time, A) neat CARILON Polymer and B) a blend of CARILON Polymer and 15 percent novolac resin.

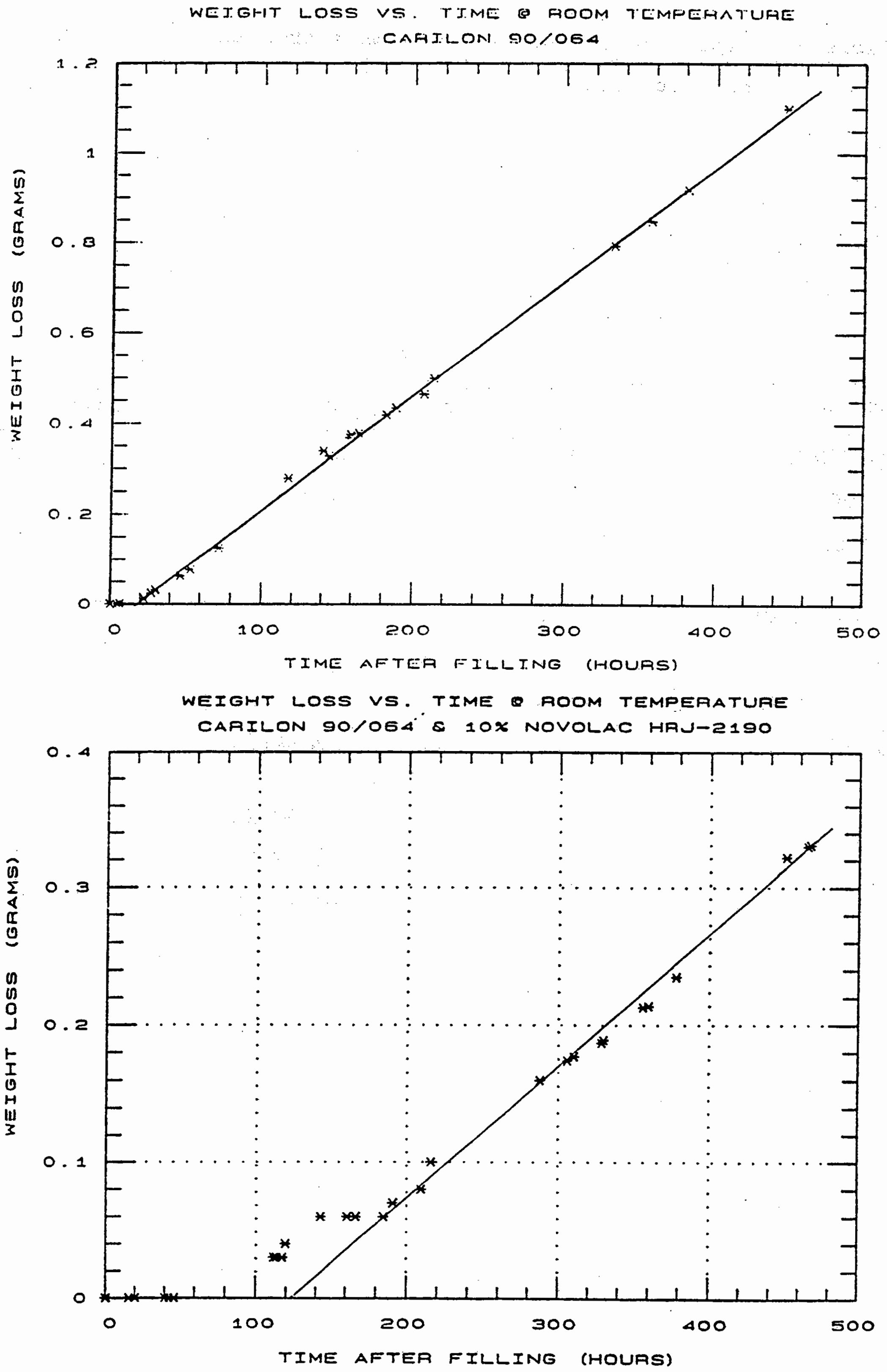


Figure 2 Reduction of water permeability in polyketone cups after retort as a function of novolac content.

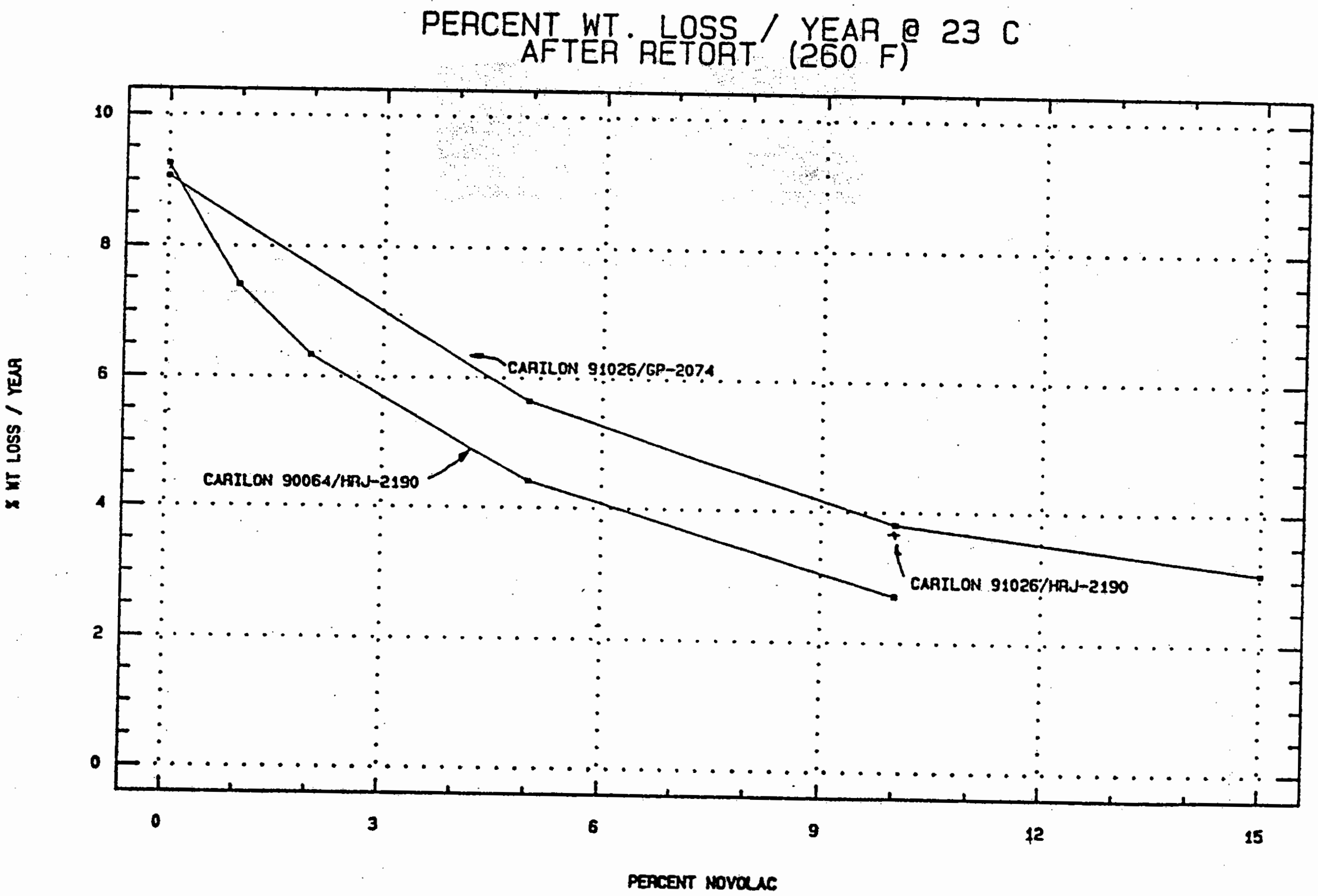


Figure 3 Reduction of water permeability in polyketone cups after retort as a function of polyvinylphenol content.

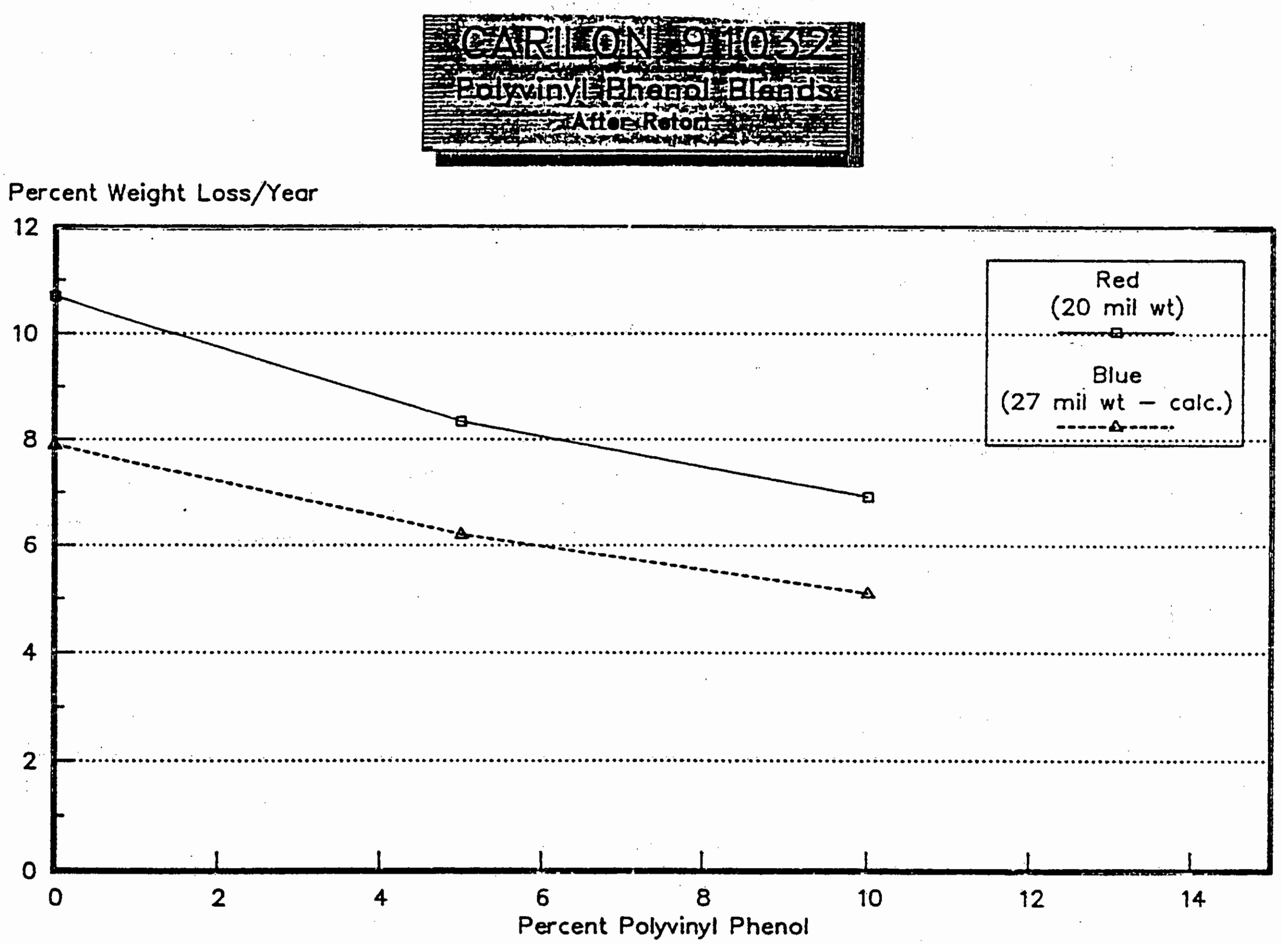


Figure 4 Water absorption of polyketone blends as a function of novolac content. A) First immersion. B) Dried, then second immersion.

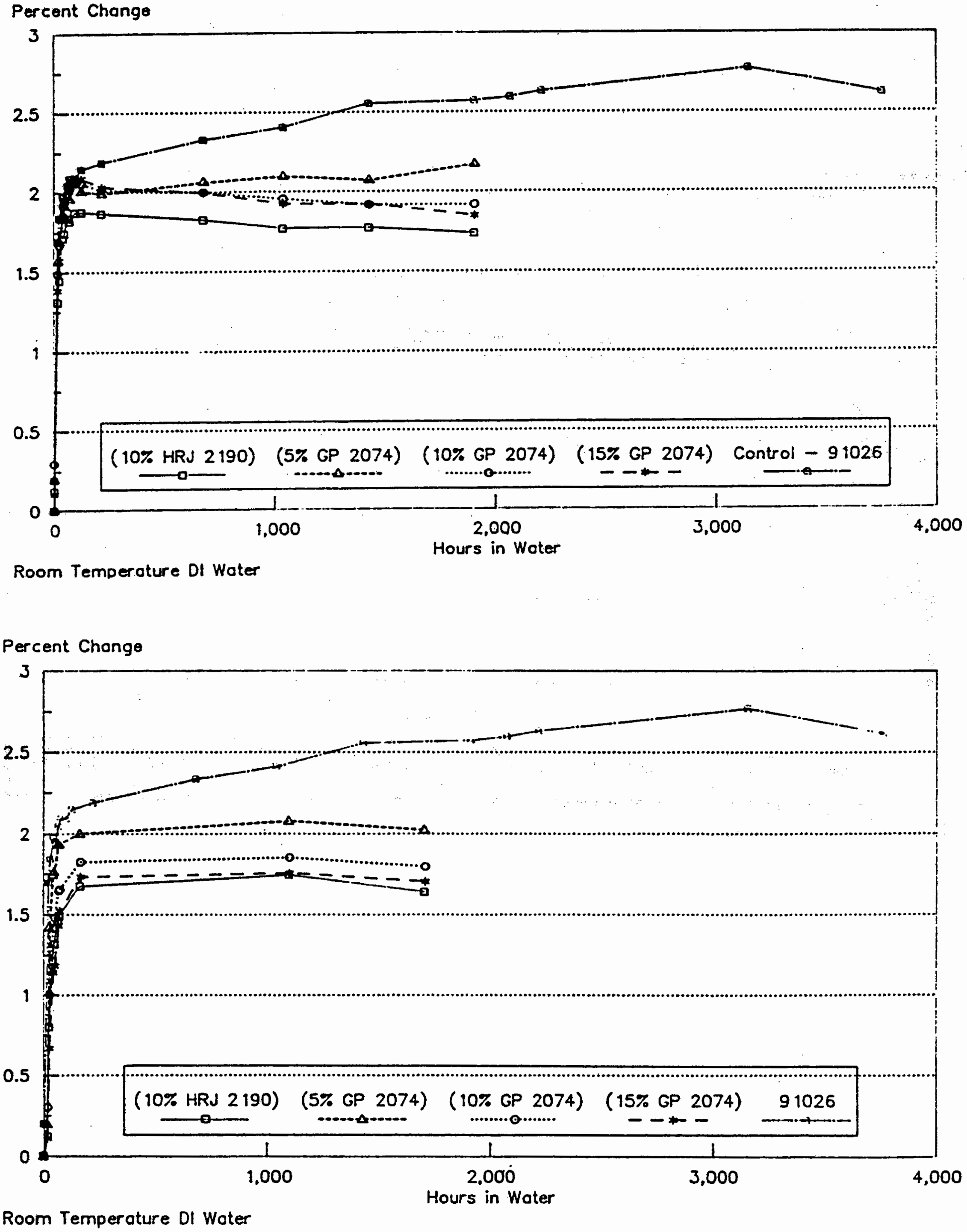
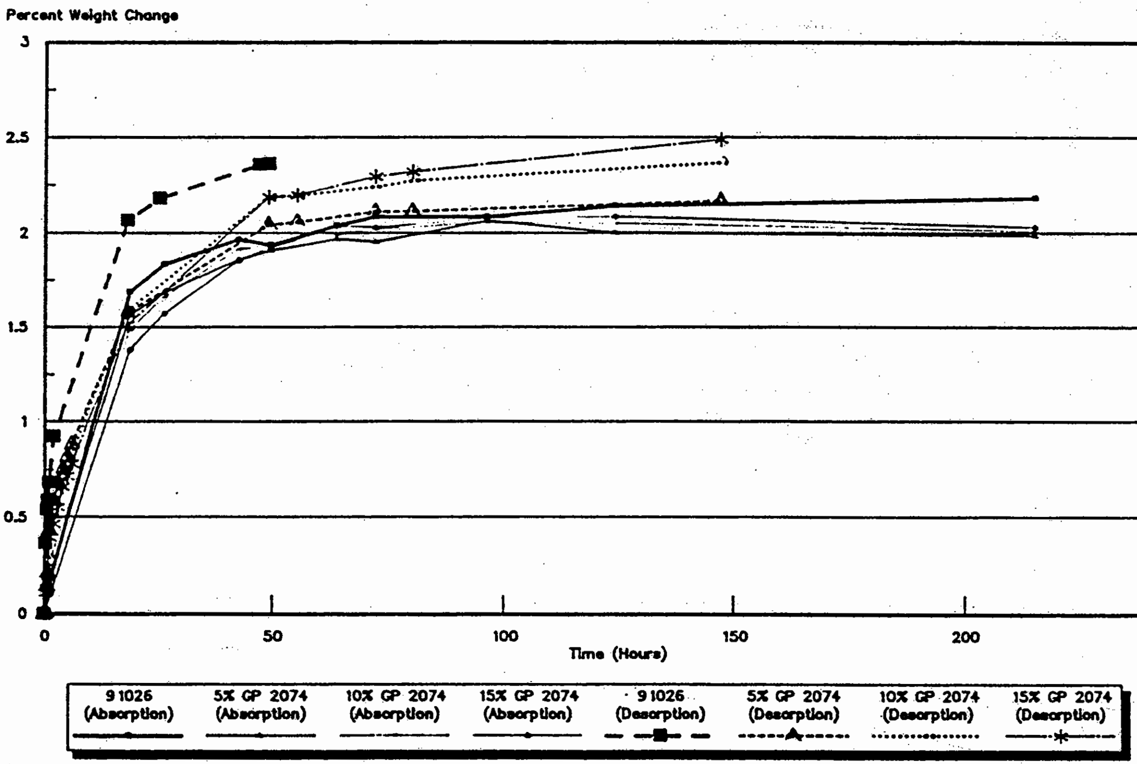


Figure 5 Water desorption (compared to absorption) versus time for polyketone blends.



1. Absorption in RT Water
2. Desorption in desiccator at ambient temp.

Figure 6 Desorption coefficient of polyketone blends as a function of time.

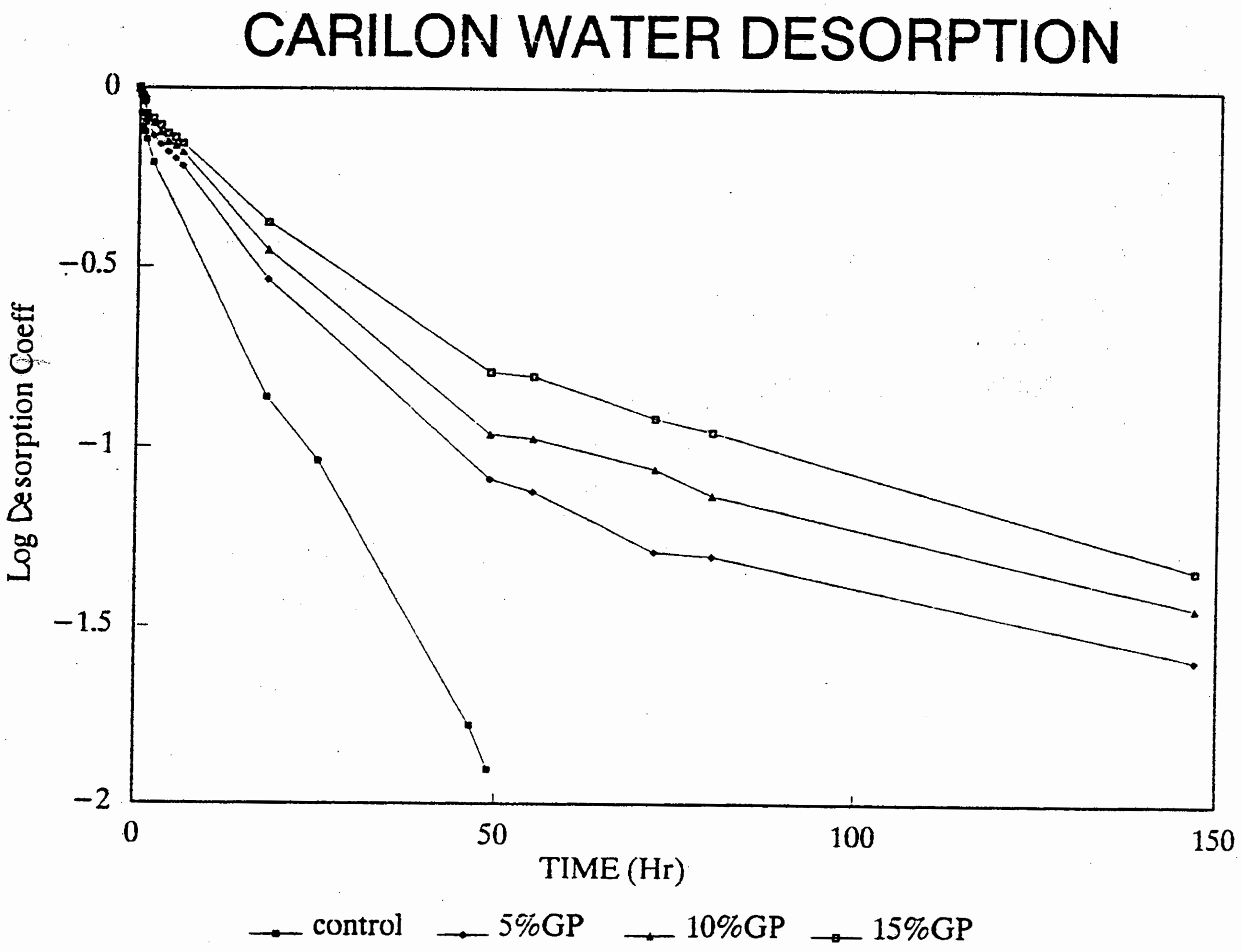


Figure 7 Dynamic mechanical storage modulus of polyketone blends as a function of novolac content.

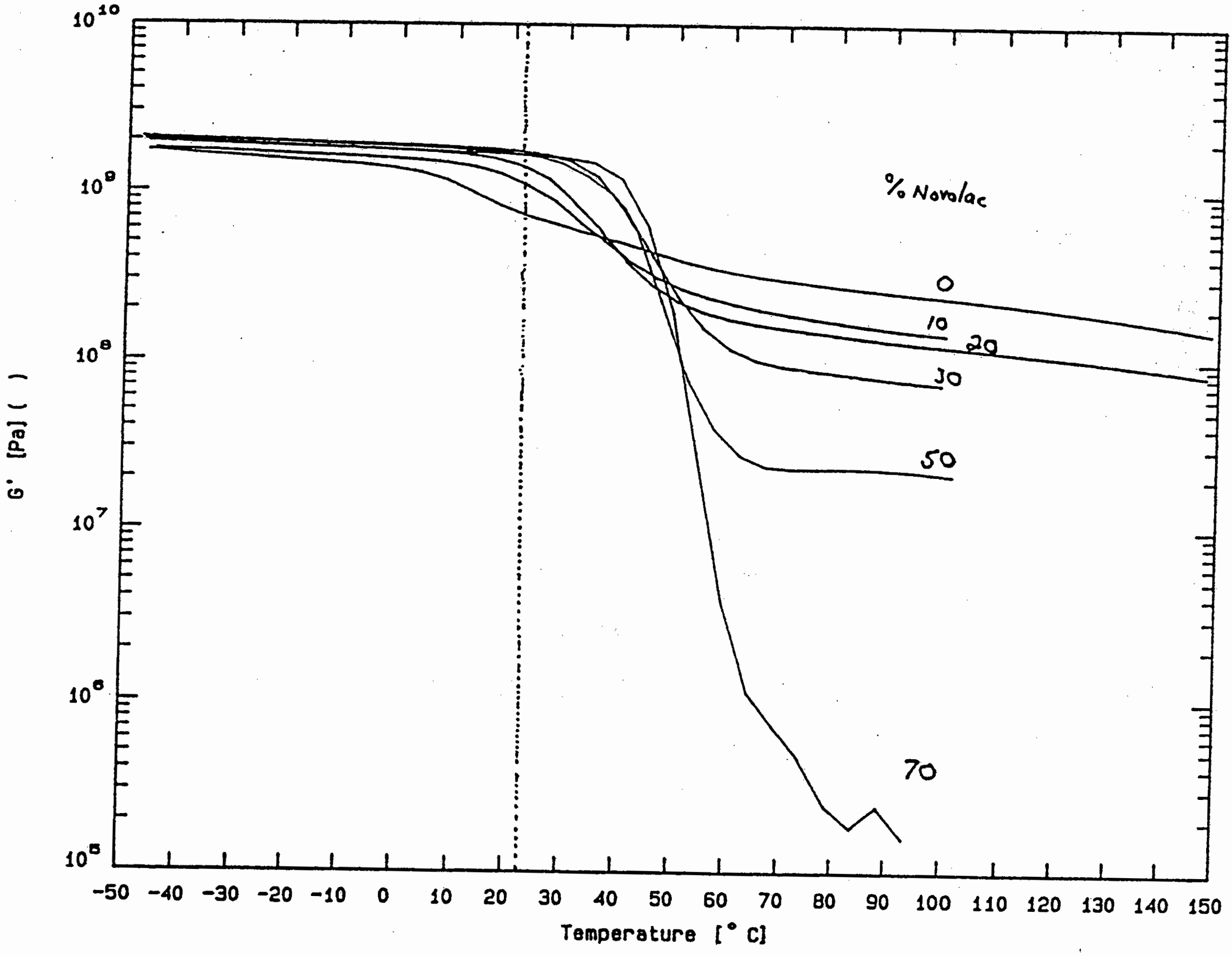
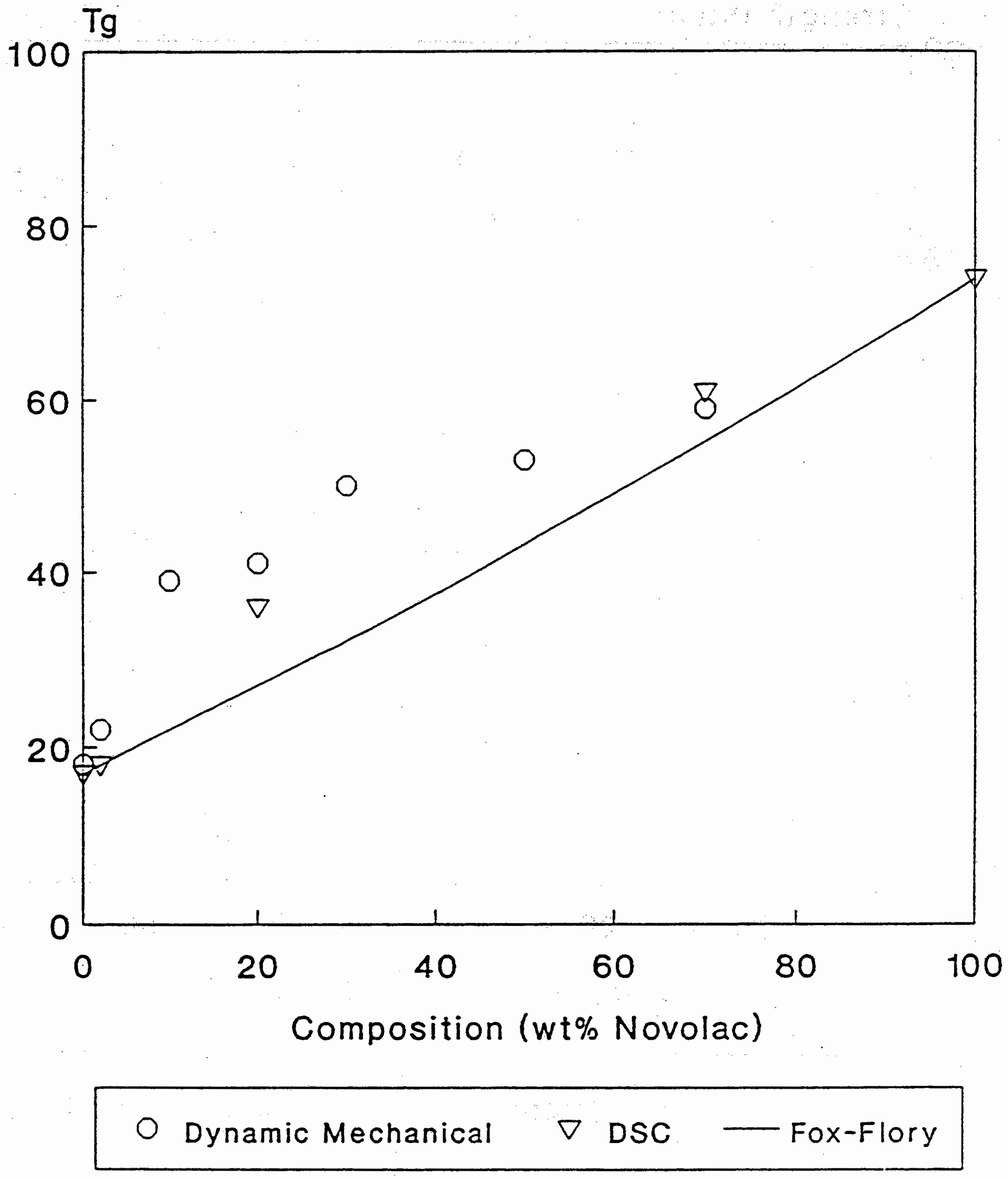
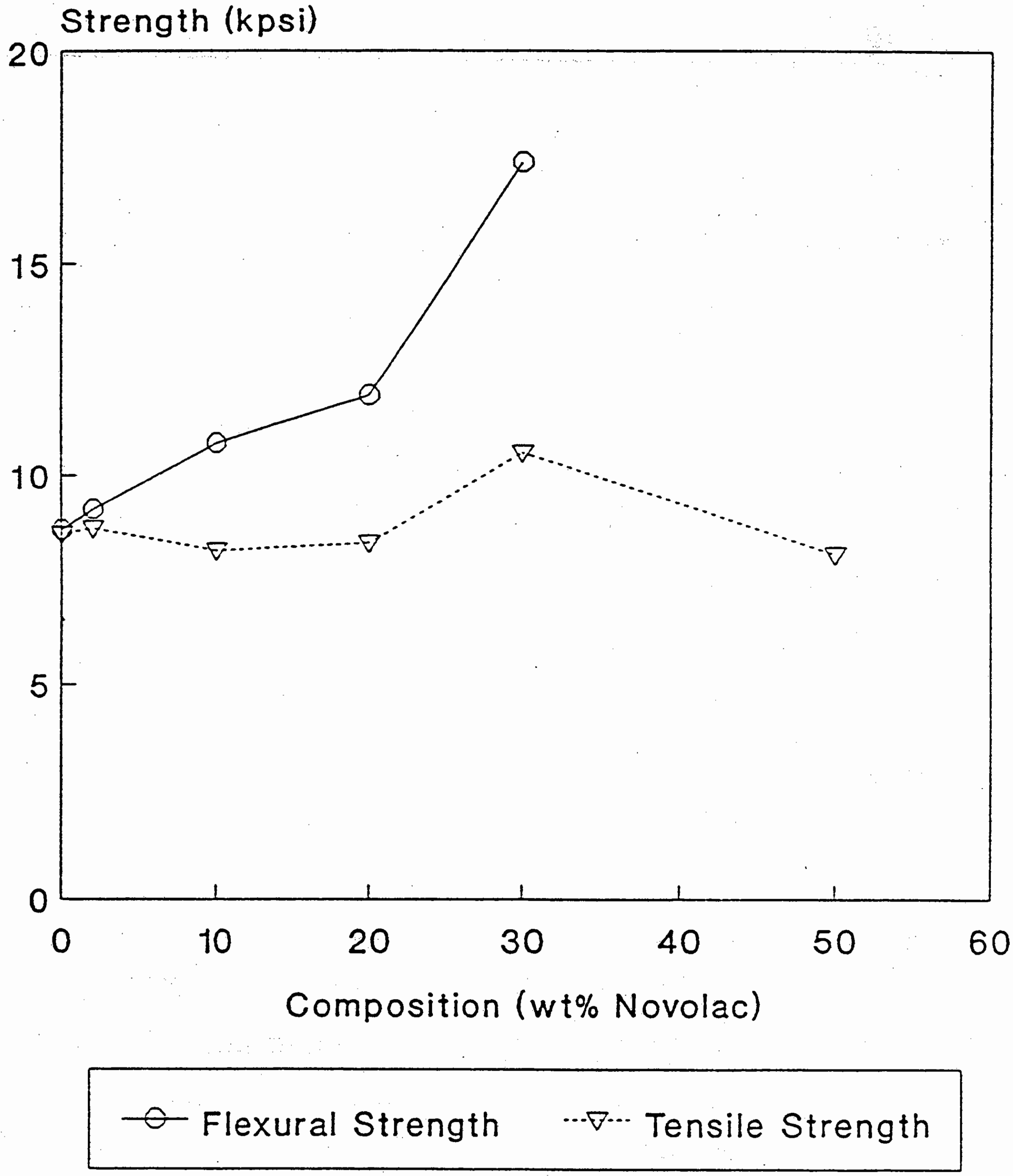


Figure 8 Glass transition temperature of polyketone blends as a function of novolac content.



P-1000/2 / HRJ-2190 Blends

Figure 9 Strength of polyketone blends as a function of novolac content.



Room temperature, Dry as molded
HRJ 2190/P-1000/2 Blends

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