Polymers are considered to be moderately thermally stable, if they survive incremental increases in temperature in an inert atmosphere without a significant change in properties (Table 9.1).

Plastics which meet these requirements have the following structural characteristics:
- high proportion of heterocyclic or aromatic rings
- high bond energies between the atoms
- high cohesive strength between the polymer chains
- oxidation resistant bonds.

Phenolic resins possess these prerequisites to a considerable extent. Although non-modified, inorganically filled phenolics are already considered temperature resistant, their thermo-oxidative resistance can be further improved by chemical modification 3.

The weak point of phenolic resins is the oxidative susceptibility of the phenolic hydroxyl group and the methylene linking group. Poly-p-xylylene is known for its excellent high temperature stability.

\[
\begin{array}{c}
\text{CH}_2 - \text{O} - \text{CH}_2 \\
\end{array}
\]

(9.1)

The following methods are utilized to improve the thermo-oxidative resistance of phenolic resins:
1. Etherification or esterification of the phenolic hydroxyl group,
2. Complex formation with polyvalent elements (Ca, Mg, Zn, Cd, ...)
3. Replacement of the methylene linking group by heteroatoms (O, S, N, Si, ...)

| Table 9.1. Guidelines for rating of plastics as thermally resistant\(^1\) |
|------------------------|-----------------|
| \(\degree C\) | Hours |
| 175 | 30,000 |
| 250 | 1,000 |
| 500 | 1 |
| 700 | 0.1 |

| Table 9.2. Thermal resistance of phenol resols as related to temperature and time\(^3\) |
|------------------------|-----------------|
| \(\degree C\) | Time |
| 1,000–1,500 | Seconds |
| 500–1,000 | Minutes |
| 250–500 | Hours |
| < 200 | Years |

A. Knop et al., *Phenolic Resins*
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The most important general modification reactions in phenolic polymer chemistry are the etherification (O-alkylation) and C-alkylation (Friedel-Crafts) reactions\(^4\). Both reactions are commonly used to enhance flexibility and compatibility with polymers and solvents and to adjust reactivity and performance. Because of the strong nucleophilic activity of the phenolic group, mild catalysts and operating conditions are usually employed for alkylation with olefins. However, the easy formation of ethers, especially during mild conditions, and the tendency of the hydroxyl group to complex the catalyst must be considered. Diisobutylene, terpenes and tung oil are the olefins most frequently used (see 14.1.1, 18.1, 19.4).

### 9.1 Etherification Reactions

The hydroxymethyl group in phenols and phenol prepolymermers can easily be etherified (9.2) with alcohols because of their tendency to form hydroxybenzylcarbocation ions. High hydroxymethylated phenols and an excess of alcohol are used to avoid the self-condensation reaction.

In general the reaction is performed at pH 5-7 and at temperatures between 100–120 °C with monoalcohols like methanol, butanol and isobutanol. Butanol is most frequently used; water is separated via azeotropic distillation with an excess of butanol\(^5\). Such etherified resols exhibit a higher solubility in aromatic solvents and improved flexibility. They are used mainly in coatings, impregnating resins for electrical laminates and adhesives. Their reactivity, however, is reduced. Also polyhydroxy compounds are recommended for flexibilization, e.g. glycol, glycerine, polypropylene glycols, hydroxypolyesters and polyvinylacetals.

On the other hand, the etherification of the phenolic hydroxyl group (O-alkylation) (9.3) leads to improved alkali resistance. Better flexibility, light fastness and with allyl compounds, enhanced air drying properties are also obtained. The reactivity of phenol ethers towards formaldehyde is drastically reduced in comparison to phenols. Therefore, the resol is first prepared and the phenolic hydroxyl group etherified (alkylated) with stronger electrophiles, e.g. allyl chloride, alkyl bromides, alkyl sulfates, epichlorohydrin and epoxide compounds in the presence of sodium hydroxide. In general, mild conditions are necessary to avoid polymer formation and C-alkylation.

Novolak resins can also be O-alkylated for higher performance. Resins with improved light fastness, which are soluble in alkali, are obtained by O-alkylation with monochloroacetic acid.

\[
\begin{align*}
\text{(9.2)} & \quad R = H, \text{CH}_3\text{OH}, \text{CH}_2X \\
\text{(9.3)} & \quad \text{CH}_2\text{OH}
\end{align*}
\]

Allyl prepolymermers, produced by O-alkylation with allyl chloride can be used as additives for can and drum coatings, and for electrodepositive paints based on epoxy-, polyvinylacetel- or polybutadiene resins because of their increased thermooxidative stability, excellent resistance to chemicals and relatively good flexibility\(^6\).