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論文名稱: 可交聯型樹脂之表面性質探討

英文論文名稱: Investigation on the Surface Property of Curable Resins

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酯化酚醛環氧樹脂、表面自由能、接觸角；

英文關鍵詞: curable, crosslinked, resin, cresol novolac epoxy,

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contact angle

[摘要]

不同結構特徵的可交聯型之丙烯酸酯化甲基酚醛環氧樹脂衍生物可經接觸角的量測及表面自由能理論來探討該可交聯型樹脂的表面性質與不同結構之關係。

甲基酚醛環氧樹脂(Cresol novolak epoxy resin ; CNER)與含有飽和或不飽和單羧酸進行反應(全部或部份)開環酯化，可得具有烯基及羥基之光可硬化及熱可硬化的丙烯酸酯化甲基酚醛環氧樹脂(acrylated cresol novolac epoxy resin; ACNER)或冰醋酸酯化甲基酚醛環氧樹脂(acetylated cresol novolac epoxy resin; AcCNER)或冰醋酸搭丙烯酸酯化酚醛環氧樹脂(acetylated/acrylated cresol novolac epoxy resin; AmixCNER)。將所得之 ACNER 中的羥基再與飽合或不飽合多元酸酐(saturated or unsaturated polybasic acid anhydride)進行(全部或部份)酯化反應，反應後產生的樹脂為含有烯基、羥基、及羧酸基之可交聯型預聚物(carboxylated curable oligomers; acidified ACNER; HACNER)；或者將所得之 ACNER 中的羥基再與單元酸酐(monobasic acid anhydride)進行(全部或部份)酯化反應而將羥基包封(capping)，反應後產生的樹脂為含有烯基但不含羥基之可交聯型預聚物(acetylated curable oligomers; capped ACNER; CACNER)。所合成之樹脂利用 FTIR 及 $^1\text{H NMR}$ 作結構的鑑定。各可硬化型化環氧樹脂

衍生物經由塗佈及乾燥成膜，其後可再經 UV 光照射進行光固化反應而得固化膜，並利用 DSC 及 FTIR 說明可交聯型樹脂的可光固化性。光固化前後之樹脂薄膜可經由接觸角之量測，再經由二液體幾何均法 (Two-Liquid Geometric Method) 及三液體酸鹼法 (Three-Liquid Acid-Base Method)，可計算出可交聯型樹脂表面的自由能與分子間所產生之極性能參數 (γ^d 、 γ^p 、 γ^s 、 γ^+) 及非極性能參數 (γ^d 、 γ^w)。結果顯示在樹脂結構中羥基極性基團之貢獻能夠提高極性能參數 (γ^p 及 γ^s)，即提高樹脂表面極性。可交型樹脂表面皆接近單極性表面 (Lewis 鹼， γ^+)；而樹脂結構中含有羧酸基團能夠提高 Lewis 酸參數 (γ^+)，即提高樹脂表面的電子接受特性。除此之外，可交聯型樹脂經光固化後，會降低 γ^d 、 γ^s 及 γ^w 值，當交聯密度愈大會導致 γ^d 及 γ^s 值下降，因而降低總固體表面自由能 (γ^s)。

[英文摘要]

Curable acrylated cresol novolac epoxy resin derivatives with different structural features were synthesized, and the relationship between the surface free energy and different structures of curable resin were studied through contact angle measurement and surface free energy calculation. The uv/thermal-curable acrylated (or acetylated) cresol novolac epoxy resins (ACNER, AcNER, AmixCNER) containing vinyl and hydroxyl groups were first obtained from the esterification of saturated or unsaturated monocarboxylic acid with N-695 cresol novolac epoxy resin (CNER). Carboxylated curable resins (acidified ACNER; HACNER) containing vinyl, hydroxyl and carboxyl groups were then obtained by esterification of hydroxyl groups of ACNER with saturated or unsaturated polybasic acid anhydride, and acetylated curable resins (capped ACNER; CACNER) mainly containing vinyl groups were obtained by esterification of hydroxyl groups of ACNER with monobasic acid anhydride. The esterification and structure of synthesized resins were characterized by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR).

The curable resins films for contact angle measurement were prepared by coating and then drying. The cured films were obtained after UV irradiation. The photo-curable properties of synthesized resins can be characterized by DSC and FTIR.

Surface free energy of curable resins (ACNER、HACNER、CACNER) before and after curing was respectively calculated using two-liquid geometric and three-liquid acid-base methods through contact angle measurement, and evaluated in terms of various surface free energy components (γ^d , γ^p , γ^{LW} , γ^- , γ^+ , AB).

The experimental results showed that an increase in the amounts of hydroxyl group of the derivative resins results in increase in the polar component of surface free energy (γ^p , γ^-), indicating the increase of

polarity of resin surface. The surface of curable resins (ACNER、

HACNER、CACNER) surface was found to be monopolar (Lewis base、

—). Further, the Lewis acid component (+) of the surface free energy of curable resins increases with an increase of carboxyl group content, indicating the increasing electron accepting character of the surface. Furthermore, results also showed that the —, p, and s of curable resins decrease with the increase of density of crosslink through UV curing.