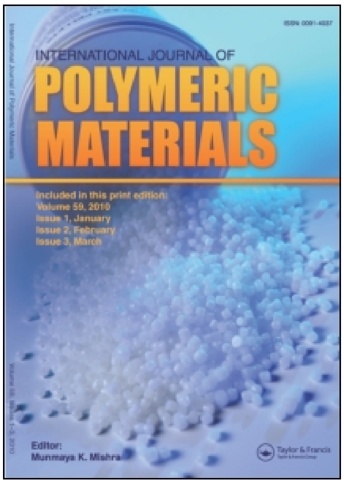

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Hyperbranched Polyether as a Modifying Agent for Urea-Formaldehyde Resins—Hardness and Strength Control Tool

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A commercially available urea-formaldehyde (UF) resin was blended with a hyperbranched polyether (HBP) obtained from glycerol being a by-product in biodiesel production. The mechanical properties of the cured polymeric blends are described in this article. It was found that low addition (3 wt%) of the modifier significantly improves the hardness (16%) and the compressive shear strength (17%) of the polymer, whereas water absorption remains unaffected. It was also shown that blending UF resins with hyperbranched polyethers can be an effective tool for controlling mechanical properties and dimensional stability of the polymeric systems.

Keywords: hardness, hyperbranched polymers, shrinkage, UF resin

INTRODUCTION

Urea-formaldehyde resins (UFs) are produced in amounts exceeding 5 million metric tons annually. They are thermosetting resins, not only used as adhesives in wood and furniture industry, but also as lacquers or bulk molding compounds. In order to enhance their mechanical, adhesive and physiochemical properties, intensive research on UFs

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modifications has been carried out for decades. Deppe and Ernst [1] studied properties of urea-formaldehyde-melamine-formaldehyde blends. Azarow et al. [2] replaced ammonium chloride with a product of condensation of epichlorohydrine and diphenylamine as a hardener. Sulfur-modified urea-formaldehyde resins were investigated by Meyer et al. [3]. Recent modifications are aimed at increasing water resistance, processing improvement, avoiding self-cure during storage and transportation [4] or lowering formaldehyde emission [5]. A wide spectrum of compounds was applied as modifying-agents: aliphatic amines [6–8], dialdehydes [9–10], latexes [11], emulsifiable methylene diphenyl diisocyanate (EMDI) [12]—to name just a few. However—according to the authors' knowledge—no modification of a UF resin with hyperbranched polymer (HBP) has ever been reported.

Dendritic and hyperbranched polymers with terminal functional groups represent a new class of polymeric compounds that attracts attention of many research groups. This class of macromolecules is reported in the literature to be effective tougheners for thermosetting resins, such as epoxies [13], bismaleimide [14], and vinylesters [15]. Results reported by these authors are interesting and promising.

It was hypothesized that the addition of HBP to UF resin would affect and enhance the mechanical properties of the cured UF/HBP blends.

Thus, in this study an attempt to employ hyperbranched polyether with hydroxyl end groups—suitable for condensation with the UF resin—as an additive has been undertaken. Performance of the polymer and its properties were investigated.

EXPERIMENTAL

Materials and Instrumentation

Commercially available urea-formaldehyde resin with U/F molar ratio = 1 : 1.3, content of solids 65 wt% and viscosity at 20°C of 230 mPas was kindly donated by Zaklady Azotowe "Kedzierzyn" SA (Kedzierzyn-Kozle, Poland). Hyperbranched polyether (m.w. 875 g/mol, viscosity of 20.5 Pas at 50°C) with hydroxyl terminal groups was prepared according to the procedure reported elsewhere [16]. Ammonium chloride solution was prepared using distilled water. Ready-to-use blend formulations were prepared in tap water. Viscosity was measured on METTLER RM180 Rheomat (Mettler-Toledo, Columbus, OH). Brinell hardness was measured on Lucznik PW-106 (Zakłady Metalowe im. gen. Waltera, Radom, Poland) instrument.

TABLE 1 Blend Formulations—Percent of Total Composition Weight

Entry	Resin, %	HBP, %	NH_4Cl, %	Water, %
1[a]	80.6	—	3.0	16.4
2	80.6	3.0	3.0	13.4
3	80.6	6.0	3.0	10.4
4	80.6	9.0	3.0	7.4
5	80.6	15.0	3.0	1.4

[a] Control polymer.

Compressive shear strength measurements were performed on Heckert FP 10 (VEB Thüringer Industriewerk Reuenstein, Chemnitz, Germany) instrument with 60 mm/min shear rate. Statistical analysis was performed on R Programm (Development Core Team (2005). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0, URL http://www.R-project.org). The statistical significance was evaluated by p-values calculated in the Student t-test with 95% confidence interval.

Blend Preparation

UF/HBP blends with 3, 6, 9, 15 wt% of HBP (Table 1) were prepared as aqueous solutions according to the following procedure: to a weighted portion of the resin, calculated amounts of hardener (10% NH_4Cl aqueous solution) and water were added. The mixture was stirred 1 min (mixer speed 60 rpm) then the required amount of HBP was added and stirring was kept another 4 min.

Curing Conditions

Bar-shaped samples (70 × 20 × 20 mm) for shear strength and hardness tests were die-casted and cured for 3 h at 70°C, then contitioned for 72 h at 20°C. A minimum of 5 specimens were tested in each series.

Water Absorption

Weighted samples of cured polymer (70 × 20 × 20 mm) were immersed in water at ambient temperature for 24 h. After that time samples were weighted again. Water absorption was calculated by using the formula:

$$A\% = \frac{m_1 - m_0}{m_0} \times 100$$

in which m_1 is the weight of sample after soaking, m_0 is the weight of dry sample.

RESULTS AND DISCUSSION

Compressive Shear Strength

Figure 1 clearly shows that shear strength of the cured polymer depends on the amount of HBP used in the composition. The maximum strength—17% increase with respect to control polymer—was achieved for 2–3 wt% of the modifier. Higher fractions of HBP in the blend result in strength lowering, which can be ascribed to two opposite effects that counterbalance each other. On one hand, hyperbranched polymer acts like a multifunctional crosslinker providing (1) higher crosslink density, (2) formation of the hydrogen bonds between HBP hydroxyl group and C=O of urea, which results in higher stiffness and strength. On the other hand, when critical HBP concentration is exceeded, it acts like a plasticizer introducing some flexibility into the network and lowering its compressive strength.

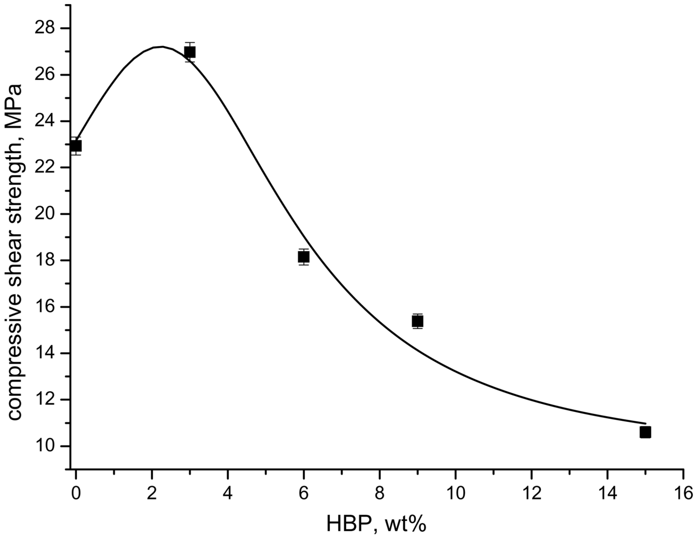

FIGURE 1 Compressive shear strength vs. HBP content in the blend.

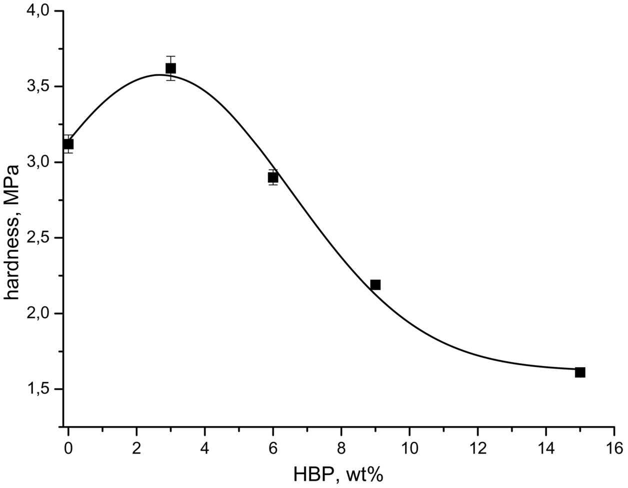

FIGURE 2 Brinell hardness vs. HBP content in the blend.

Compressive shear strength dependence on the HBP content in the blend is coherent with hardness analysis shown in Figure 2, where maximum of the hardness is observed for 3 wt% HBP content, too. However, gain in compressive strength is connected with significant shrinkage occurrence (Table 2, entry 2)—p-values < 0.05.

Hardness Measurements

Hardness measurements were based on the Brinell method. Diameter of the ball intender was 10 mm, applied load was 600 N. The results are presented in Figure 2. Up to 3 wt% of HBP in the composition, the hardness increased to achieve in that point 16% enhancement

TABLE 2 Mean Values of Linear Shrinkage (S_L%) and Volumetric Shrinkage (S_V%)—Standard Deviations Given in Parentheses

Entry	S_L%	S_V%	S_L%, p-value[b]	S_V%, p-value[b]
1[a]	7.03 (0.18)	19.53 (0.16)	—	—
2	7.78 (0.33)	21.73 (0.39)	0.0381	0.0052
3	8.50 (0.54)	23.16 (0.34)	0.0032	0.0001
4	7.54 (0.65)	20.99 (0.63)	0.3091	0.0552
5	3.28 (0.47)	9.52 (1.31)	0.0021	0.0050

[a] Control polymer.

[b] p-values are calculated with respect to control polymer. Significance level $p < 0.05$.

with respect to the control polymer. The observed toughness enhancement can be explained by the hyperbranched polyether mode of action, which—up to 3 wt%—acts like a multifunctional "co-hardener" forming upon curing inhomogeneity centers (hard knots) within the polymer network.

The compositions with 4 or more wt% of HBP in the blend show subsequent decrease in hardness of the polymer—even below the control composition. It is supposed that, as for the compressive strength, the hardening effect is overwhelmed by the plasticizing effect, so that decrease occurs.

Water Absorption

Measured changes in water absorption are statistically insignificant (calculated p-values > 0.05), so it can be recognized as constant. UF resins are generally highly hydrophilic, so it is intuitively obvious that incorporation of hydrophilic hyperbranched polyether molecules into the network will not result in a decreased hydrophilicity. The obtained results, shown in Figure 3, confirm that assumption.

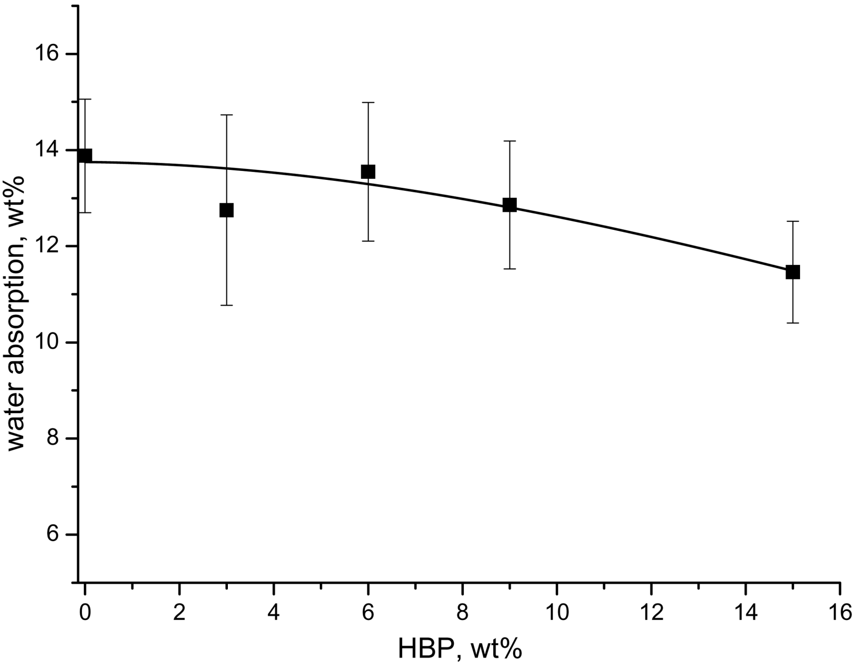

FIGURE 3 Effect of HBP content on water absorption of the cured polymer.

Polymerization Shrinkage

Polymer shrinkage measurements were performed on bar-shaped samples (70 × 20 × 20 mm). Linear shrinkage on polymerization was calculated by using the formula proposed by de Gee et al. [17]:

$$S_L\% = \frac{\Delta L}{L + \Delta L} \times 100$$

in which ΔL is length loss in mm and L + ΔL is equal 70 mm. The volumetric shrinkage was derived from the linear shrinkage:

$$S_V\% = 3S_L\% - 0.03(S_L\%)^2 + 0.0001(S_L\%)^3$$

where the last term is negligible.

The volumetric shrinkage is proportional to the linear shrinkage, because $S_V\%$ values are calculated directly from $S_L\%$.

As it can be seen in Figure 4, maximum of volumetric shrinkage occurs for the formulation with 6 wt% HBP content and is 2.2% higher than that for the control polymer. The formulation with 15 wt% content of the modifier exhibits dimensional stability better than the control polymer–volumetric shrinkage at 9.5%-level, which is 10% lower than that of the control. Thus, it has been shown that addition

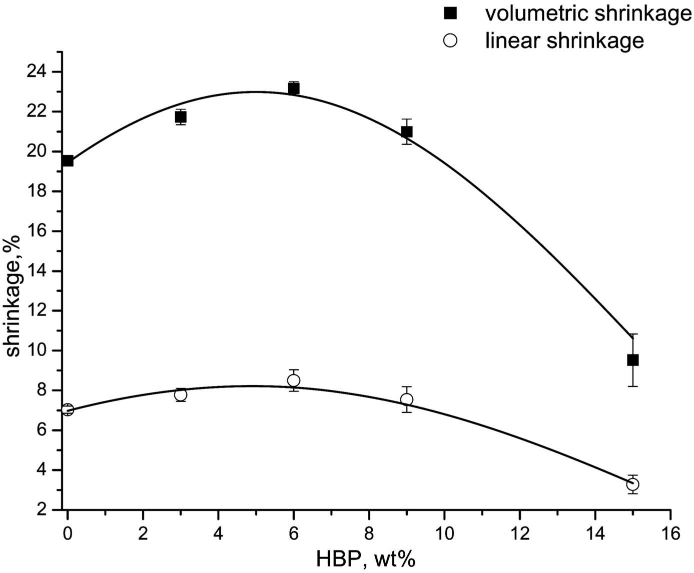

FIGURE 4 Effect of HBP content on linear and volumetric polymerization shrinkage.

of HBP to the blend allows to achieve reduced shrinkage and improved dimensional stability of the system.

CONCLUSIONS

Low hyperbranched polymer addition to a UF resin results in the improvement of hardness and compressive shear strength of the cured blend. It was also found that, for the compositions in which HBP content is higher than *ca.* 4 wt%, the plasticizing effect overwhelms the hardening effect and subsequently lowers both hardness and compressive shear strength.

Volumetric shrinkage for the best-performing formulation remains at acceptable level of 2–3% when compared to the control polymer. For the compositions with higher content of the hyperbranched polyether, despite deteriorated mechanical properties, lower linear and volumetric shrinkage occurs, thus better dimensional stability is observed.

It may be concluded that blending UF resins with hyperbranched polyethers allows to control the mechanical properties of the systems and provides dimensional stability control tool. Further investigation on application of HBP to modifying urea-formaldehyde resins seems to be worth considering.

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