

ECOLOGICALLY SAFE APPLICATIONS OF MULTICOMPONENT POLYMER SYSTEMS BASED ON HYDROPHILIZED UNSATURATED POLYESTER RESINS

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Abstract

Development of new polymer systems based on thermo-reactive resins is topical from a chemical point of view and because of the possible programmable changing their properties in order to satisfy some specific requirements. A new composition for a two-component polymer system based on a hydrophilized unsaturated polyester resin (HUPR) and melamine formaldehyde resin (MFR) was formulated. Its strength parameters were tested by dynamic mechanical, derivatographic, scanning electron microscopic and thermal analyses. The improved ecological features of HUPR/MFR were the following: preliminary water-solubility along with capacity to incorporate water (up to 50 % towards its own mass), good dilution into water during hardening, compatible hardening with other resin water dispersions, low density and relative mass, easy degradability, porosity, high strength parameters and thin-founding capacity. HUPR/MFR permits good relief impressions with high adhesion ability towards wet surfaces. It is designed for a wide application as resin plaster for casting of ornamental and building materials, flooring tiles, tiles for facing and lining, isolation layers, in the manufacture of orthopedic plaster dressings, prostheses, splints, insoles, positive-sample dental imprints and casts, etc. Replacement of conventional plaster-of-Paris materials in the building industry by HUPR/MFR-based ones could considerably reduce the risk of environmental contamination in industrialized countries.

Introduction

Polymer blends consisting of components with different properties possess, usually, some advantages over the initial polymers. The peculiarities of both structure and properties of the polymer blends composed by thermo-reactive resins remain insufficiently clarified yet. This is related to the complex processes of formation through the resins of the network of chemical bonds in the blends as a consequence of different chemical properties of the thermo-reactive materials blended (1). Development of new two-component polymer systems based on thermo-reactive resins is topical not only from a chemical point of view but also because of the opportunity for programmable changing their properties in order to satisfy some specific requirements of the purposeful application in the building, architecture, medicine and dentistry as well (2,3). Resin oligomers of different chemical nature that are not hardened can blend together without any limits because of the small molecular mass thus forming a two-phase or multi-phase material. During the hardening the blended resins can lose their mutual solubility and form disperse systems of various particle size and properties (1).

The purpose of the present work is to study the structure and to test the opportunity to obtain improved ecological characteristics of a two-component polymer system based on a hydrophilized unsaturated polyester resin (HUPR) and melamine formaldehyde resin (MFR).

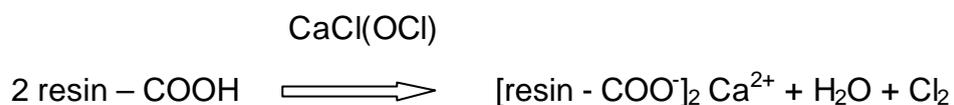
During the polymerization of the UPR the latter acquires hydrophilic properties (3) and thus the HUPR can be distinguished from the conventional compositions based on it. In this way, it can be blended at any proportion with other water resin dispersions such as MFR. The blends of HUPR with MFR are sufficiently stable and do not stratify themselves. The process of hardening of the resin blend of modified product based on UPR and equivalent mixture of $\text{Ca}(\text{OCl})_2$ and CaCl_2 , on the one hand, and MFR, on the other hand, does not last longer than 30 minutes.

The structure of these macromolecular networks and their structural defects are the primary factors during their thermal destruction. This fact is reflected in the present two-component polymer resin, i.

e., during the heating by using of thermal analysis some essential properties of the materials can be registered. Strength parameters of polymer systems based on HUPR that are blended with amino formaldehyde resins in different ratios represent a confirmation of the results from thermal examinations (4). The new material obtained by joint hardening of HUPR and MFR surpasses the building or medical plaster of Paris with respect to strength parameters and, at the same time, possesses much less density than them (3). It has been proved that this material becomes completely inert towards human skin (5) and seems appropriate for application in medical and dental practice. That is why it is of practical interest to clarify the structure and improved ecological features of these innovative, light and sound polymer composite materials.

Methods

UPR was obtained from a Vinalkid-550 P (Rouse, Bulgaria) industrial product. The hydrophilization of UPR was carried out at room temperature in the presence of 1 % - 20 % of the alkaline substance $\text{CaCl}(\text{OCl})$ (3). Under the influence of this substance the carboxylic groups in the resin turn into carboxylate anions that changes the conformation of the macromolecules and results in HUPR production. This process can be expressed with the following schedule:



This HUPR was hardened by means of conventional initiator and accelerator. This process was described in detail elsewhere (3). The blends of HUPR and MFR were obtained in two mass-percentage ratios: 90/10 and 40/60. A dynamic mechanical analysis (DMA) was carried out and the dynamic modules in the temperature range between 25°C and 140°C were read. Based on their values the tangent of the angle of mechanical losses ($\text{tg } \delta_{\text{mech}}$) was calculated. Derivatographic analyses (differential thermal gravimetric analysis, DTGA) of samples of HUPR, MFR, and HUPR/MFR in different ratios were performed using thermal gravimetric analysis (TGA) methods. Breaks from hardened samples of HUPR, MFR and HUPR/MFR in different ratios were examined under scanning electron microscope (SEM). Acute oral toxicity of HUPR in animals and skin sensitivity of HUPR in humans was previously studied (5).

Results

Figure 1 demonstrates the results from the DMA of the samples of HUPR, MFR and HUPR/MFR in the ratios of 90/10 and 40/60. An outlined maximal value is observed at $T \approx 60^\circ\text{C}$ on the temperature curves of $\text{tg } \delta_{\text{mech}}$ that can be related to the transition of the resin through the temperature of reinforcement (curve 1). The temperature dependence of $\text{tg } \delta_{\text{mech}}$ for the hardening MFR (curve 4) is more complex and presents with two peaks. This temperature behaviour is related to the more complex phase structure of the material of MFR as confirmed by the SEM study. HUPR-MFR (90/10) (curve 2) is characterized by a maximal value sufficiently close to the glass-transition temperature of both polymers. It can be concluded that HUPR phase is uninterrupted. At higher MFR concentrations (of 60%), however, there is a phase inversion difficult to interpret on curve 3.

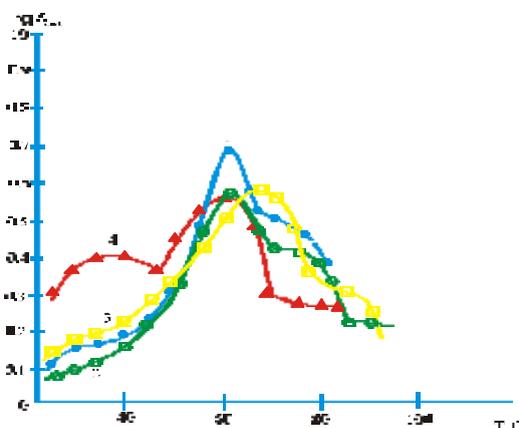


Figure 1: Temperature Dependence of $\text{tg } \delta_{\text{mech}}$ of HUPR/MFR: 100/0 (Curve 1); 90/10 (Curve 2); 40/60 (Curve 3), and 0/100 (Curve 4)

In order to clarify the peculiarity of the phase structure of HUPR/MFR (of 90/10 and 40/60 mass %) as well as to confirm the DMA data, a SEM investigation was carried out. It showed that the homogenous structure prevails in the system containing 90 % of HUPR only (Figure 2). On SEM, the surface of the break clearly demonstrates a two-phase structure with a greater amounts of MFR (90 %) as well as with HUPR/MFR (of 40/60 mass %) (Figure 3).

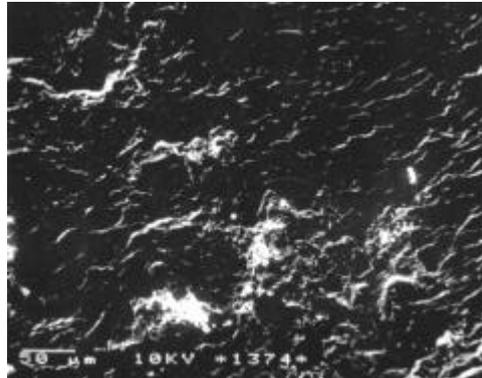


Figure 2: SEM of HUPER/MFR: 90/10 mass %

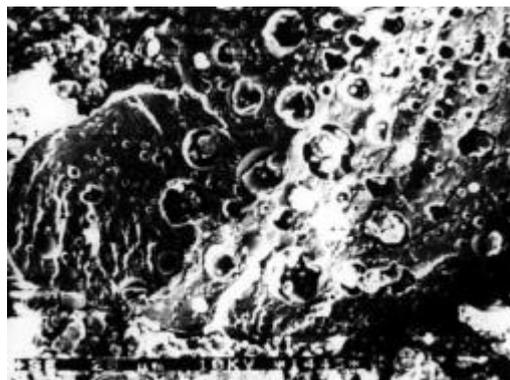


Figure 3: SEM of HUPER/MFR: 40/60 mass %

Figure 4 presents the data from the thermographic examinations of HUPR, MFR and HUPR/MFR (90/10 mass %). The parallel inspection reveals absent significant differences of thermal effects between HUPR and HUPR/MFR systems. It results from the nine-fold dominance of HUPR over MFR within the system. The changes occurring because of the 10%-participation of MFR indicate the additive contributions of the initial polymer components. The thermal destruction is particularly influenced in case of a 60%-participation of MFR in the HUPR/MFR (of 40/60 mass %) system (Figure 5). Typical of this composition is the exothermal peak of the DTGA curve at $T = 350^{\circ}\text{C}$. It is intermediate with respect to the corresponding peaks of HUPR at $T = 365^{\circ}\text{C}$ and of MFR at $T = 335^{\circ}\text{C}$.

Data from Figure 4 and Figure 5 allow the conclusion that the behaviour of the two-component polymer systems does not induce the appearance of mechanisms reducing the thermal strength of the components. The tendencies of partial mass loss in HUPR/MFR systems are caused by the presence of MFR. They are, however, insignificant below the temperature of the initialization of an intensive destruction. It is of utmost importance that HUPR/MFR system remains unaffected by any destruction within the temperature interval between 40°C and 190°C that represents the range of most common exploitation.

The joint application of DTGA, DTA, SEM and clinical methods enables the determination of such concentration ranges in which the viscose-elastic behaviour is most appropriate in respect to the materials obtained.

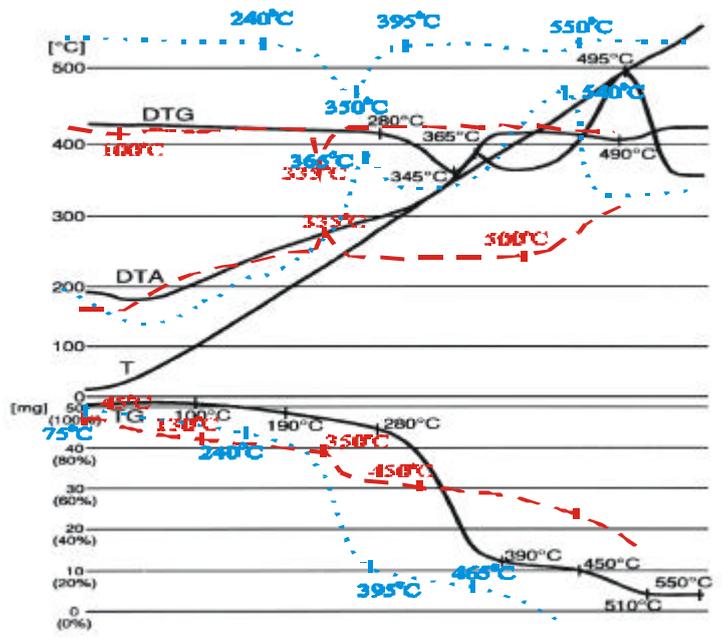


Figure 4: TGA, DTGA and DTA for HUPR, MFR and HUPR/MFR: 90/10 Mass %

Legend: HUPR _____ MFR - - - - HUPR/MFR

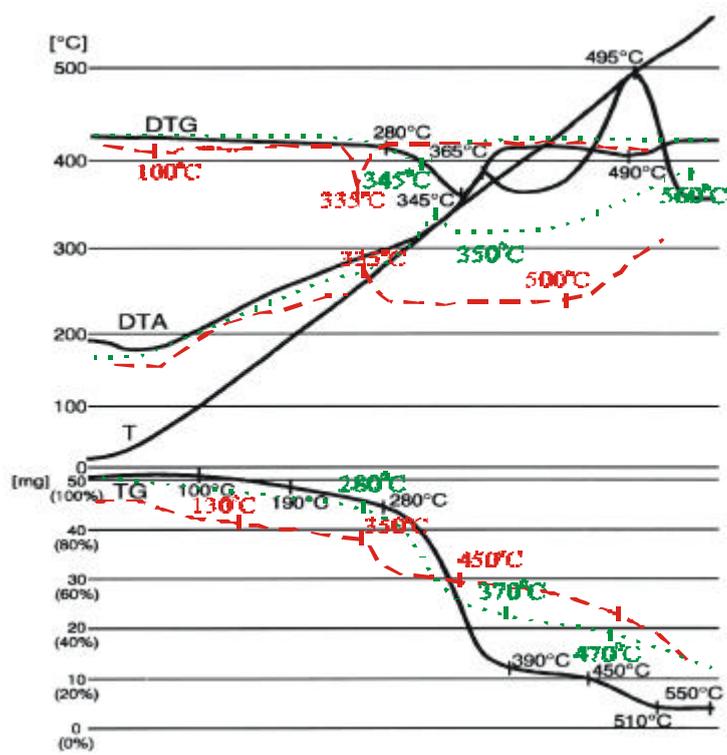


Figure 5: TGA, DTGA and DTA for HUPR, MFR and HUPR/MFR: 40/60 Mass %

Legend: HUPR _____ MFR - - - - HUPR/MFR

Discussion

Thus one can predict the elaboration of this HUPR/MFR with really improved ecological features. They can be summarized in the following way: The hydrophilic resin possesses a preliminary water-solubility along with capacity to incorporate water (up to 50 % towards its own mass) and, therefore, a good dilution into water during hardening. This makes the resin compatible when jointly hardened with other resin water dispersions. On the background of its low density, low relative mass, easy degradability and porosity it is characterized by high strength parameters and thin-founding capacity.

It has been proved that the components of polyester resins such as N-benzyl-N,N-dimethylamine (6), polyamide polyesters (7) and polyester fibers (8) exert serious hazardous effects. Here belong the occupational dermatoses among workers in fibreglass-reinforced plastics factories (9,10), the skin allergy (11), the allergic contact dermatitis in car repair work (12), etc. In this respect, HUPR/MFR as a human-friendly and ecologically safe material could successfully replace the conventional polyesters.

Conclusion

HUPR/MFR permits good relief impressions combined with high adhesion ability towards wet surfaces. This system is designed for a wide application as resin plaster for casting of ornamental and building materials, flooring tiles, tiles for facing and lining, isolation layers, in the manufacture of orthopedic plaster dressings, prostheses, splints, insoles, positive-sample dental imprints and casts, etc. Replacement of conventional plaster-of-Paris materials in the building industry by HUPR/MFR-based ones could considerably reduce the risk of environmental contamination in industrialized countries.

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