PLASMA–AIDED SURFACE TECHNOLOGY FOR MODIFICATION OF MATERIALS REFERRED TO FIRE PROTECTION

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There has been considerable interest in dielectric barrier air discharge at atmospheric pressure and room temperature over the past decade due to the increased number of industrial applications. New plasma-aided capillary impregnation technology for flame spreading stop and fire protection of porous materials was developed. Research, based on thermogravimetric analysis (*TGA*), differential thermal analysis (*DTA*), and differential scanning calorimetry (*DSC*), proves that plasma-chemical surface pre-treatment exert material change on chemical interaction between phosphorus containing flame retardant and wood matrix (*Pinus sylvestris*, Bulgaria; *Pseudotsuga*, Canada).

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1. INTRODUCTION

Diverse applications of non-thermal atmospheric pressure discharges plasma demand a solid physical and chemical understanding of the operational principals of such plasma-aided processes, [1, 2].

The plasma-aided flame retardation has been developed as a result of a new plasma aided process: the plasma aided capillary wood impregnation with flame-retardant (*FR*) water solution, which evolved as a fire protection process for wood, using original phosphorous flame retardants (*PhFRs*), manufactured by *Interior-protect, Ltd*. (*Sofia, Bulgaria*) under the trade name of *CSE-96*.

Phosphorus containing *FRs* take action efficiently in the solid phase of burning materials. When heated, the phosphorus reacts to give a polymeric form of phosphoric acid. This acid causes the material to char, forming a glassy layer, and so break down and release of flammable gases which is necessary to feed flames. By this mode of action the amount of fuel produced is significantly diminished, because char rather than combustible gas is formed. The intumescent char plays particular roles in the *FR*-process. It acts as a two-way barrier, both hindering the passage of the combustible gases towards the flame, and shielding the wood from the heat of the flame. Furthermore, the amount of fuel available for the fire is significantly diminished, because char rather than combustible gas is formed. Certain *PhFR*-products, as *CSE-96* contain phosphorus and nitrogen compounds, thus combining both the flame retarding mechanisms of phosphorus and nitrogen compounds by reinforcing their function, [3, 4, 5, and 6].

The plasma surface pre-treatment of wood by dielectric barrier discharge in air at atmospheric pressure and room temperature (*DBD*) increases the chemical activity of its surface as well as the capillary activity and improves such technological characteristics of the capillary impregnation process as the penetration depth, speed of solution spreading and adsorption, and specific quantity of adsorbed solution per unit of area. This allows using the plasma-aided retardation as a finishing process and applying it in situ, [3, 4].

Wood cell wall is thought to be a composite material made of cellulose microfibrils embedded in a water-reactive matrix of hemicellulose and lignin. The ability of the matrix to adsorb water is thus of critical importance in the water solution capillary impregnation of wood (*N. Barber* 1968). It is well-known that heat treatments and machining reduce wood hygroscopicity and chemical activity (*E. Obataya* et al. 2000) in different ways. Cold plasma pre-treatment redresses the wood surface balance, chemical and capillary activities; change the ion activity, and as result of all changes increases the impregnation ability of wood (*P. Dineff* et al. 2004), [3-6].

This study was developed as part of a large investigation on the thermal degradation of plasma-flame retarded wood (*P-FR* wood). Thermal wood degradation analysis: thermogravimetric analysis (*TGA*), differential thermal analysis (*DTA*), and differential scanning calorimetry (*DSC*), were used for evaluation the suppressing of plasma-*FR* treatment on wood pyrolysis and combustion, [7, 8].

2. EXPERIMENTAL INVESTIGATIONS

The plasma-aided *FR*-process involves two tools which are used for exerting direct impact on the thermal degradation of *FR* woods: *the first one* consists in impregnating *white pine* (*Pinus sylvestis*, Bulgaria) and *Douglas fir* (*Pseudotsuga*, Canada) woods with a water solution of *CSE-96* with 5 vol. % anionic surfactant – *FR* samples; *the second one* consists in performing cold plasma surface pre-treatment for 60 s in the plasma of *DBD* (12 kV, 10 kHz) before impregnating – *P-FR* samples, [3]. The thermal degradation of all *FR* and *P-FR* wood samples is compared with the basic samples made of natural wood – *K* samples.

Experimental conditions for all runs were as follows: thermogravimetric (*TG*), derivative thermogravimetric (*DTG*), and differential calorimetric (*DSC*) analyses were completed by *Perkin-Elmer*'s equipment in air; the heating rate was 10 ^{0}C/min (*white pine*, *WP*) and 50 ^{0}C/min (*Douglas fir, DF*), heating range from 26–36 to 600 (1200) ^{0}C was used; sample size usually was about 3.0 mg. All runs were done at least twice.

3. RESULTS AND DISCUSIONS

The thermal destruction of and chemical activity of *CSE-96* starts intensively with a mass loss at about 143 ^{0}C (2 mass %) and rapidly attains its maximum at 190 ^{0}C (*DTG*), whereas in the range 226–232 ^{0}C its mass decreases with 30 mass %, [6].

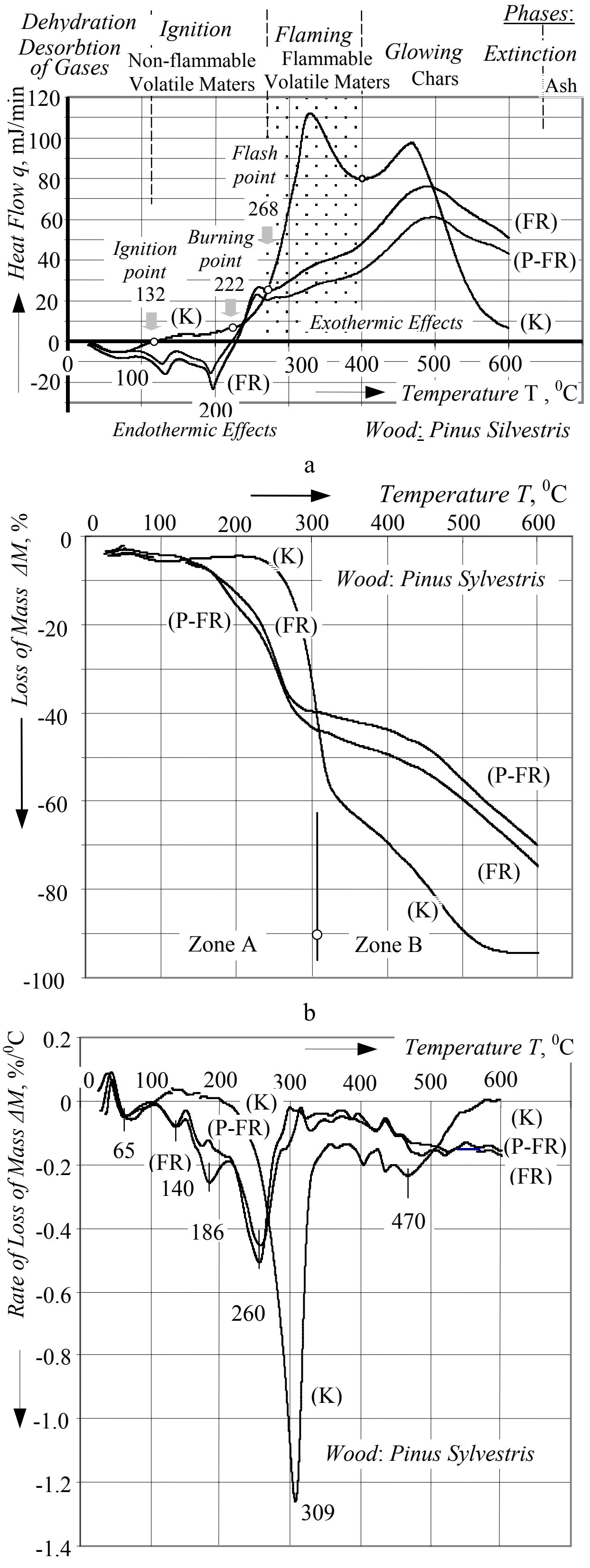

Fig. 1. Thermal analysis - DSC (a), TGA (b) and DTA (c) thermograms of white pine wood (Pinus sylvestris, Bulgaria) in air (heating rate - 10 ^{0}C per minute)

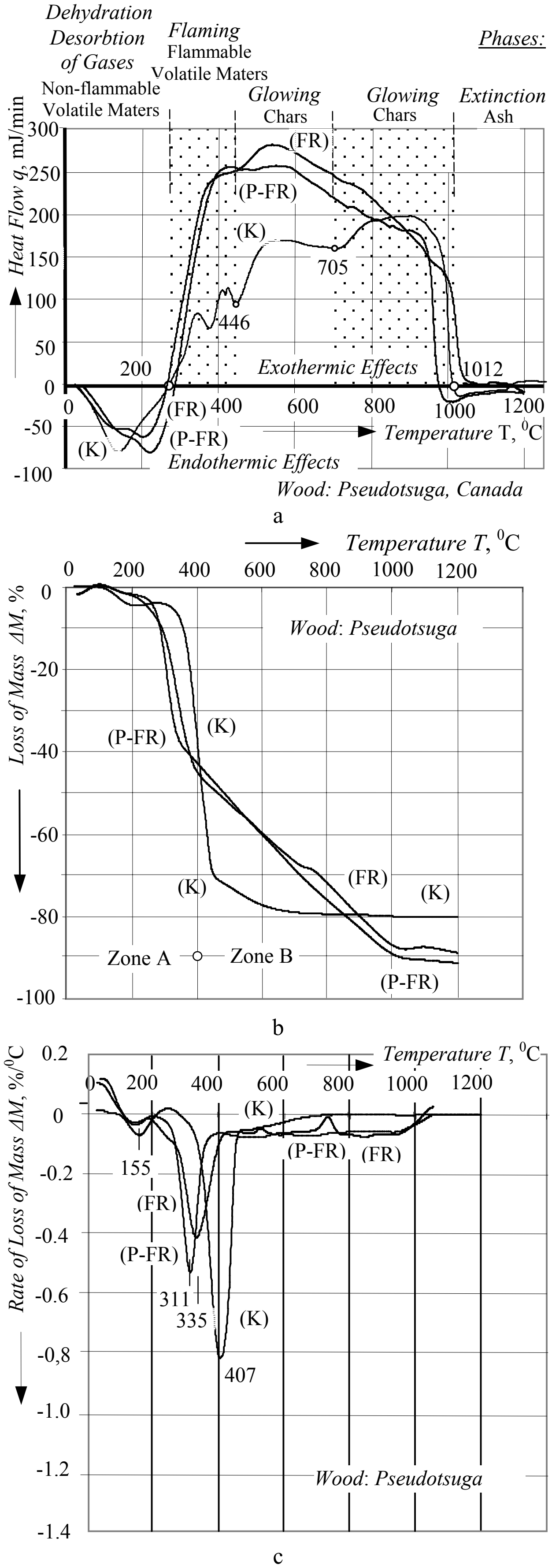

Fig. 2. Thermal analysis - DSC (a), TGA (b) and DTA (c) thermograms of Douglas fir wood (Pseudotsuga, Canada) in air (heating rate - 50 ^{0}C per minute)

The identification of typical temperature zones on the *DSC* thermograms of non-protected woods (*K* – samples) is done on Figs. 1 and 2. The flaming zones that start at ignition point (132 ^{0}C for *WP* and 272 for *DF*) and pass through different phases of growth are quite different for *WP* - 251–400 ^{0}C and for *DF* - 272–452 ^{0}C. The two kind of wood are quite different in their densities: *WP* – 370 kg/m and *DF* – 560 kg/m^3 that define different flaming behavior.

Phosphorus containing *FR* (*CSE-96*) causes the material to char very active, forming a glassy layer, and so break down and release of flammable gases which is necessary to feed flames - char rather than combustible gas is formed. The temperature zone A is the zone of glassy char layer formation pursued by very quick loss of mass (*TGA* thermograms). The maximum rate of this loss of mass was observed on the *DTA* thermograms at 260 ^{0}C (*WP*) and 311–335 ^{0}C (*DF*), Figs. 1c and 2c.

After that the build char layer stops the spreading of flame, retards and suppresses the glowing – the loss of mass in zone B is smaller than the loss of mass of non-flame retarded woods, Figs. 1b and 2b.

Plasma-aided *FR*-impregnation increases the capillary activity and improves the penetration depth, *FR*-solution spreading and adsorption, [4, 5, 6], builds more actively thick and compact char layer and retards the thermal degradation of *P-FR* wood. The improved flame retardency in comparison with the utilized capillary impregnation until now, but also realize the flame proofing at lower total exothermic effects, Figs. 1a and 2a.

CONCLUSION

As a result of the experimental investigations performed for two very different kind of wood with phosphorous containing *FR* (CSE-96) the following main conclusion can be derived - plasma-aided capillary impregnation with ionic water solution of *PhFR* (*CSE-96*), indicates not only an improved impregnation attended by increased penetration depth, spreading and absorption of *FR*-solution, but also realize better flame retardency in comparison with the utilized impregnation until now.

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ПЛАЗМЕННО-УПРАВЛЯЕМАЯ ТЕХНОЛОГИЯ МОДИФИКАЦИИ МАТЕРИАЛОВ ДЛЯ ПОВЫШЕНИЯ ОГНЕСТОЙКОСТИ

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В последнее время отмечается значительный интерес к диэлектрическому барьерному разряду в воздухе при атмосферном давлении и комнатной температуре благодаря возрастающему числу его технологических применений. Разработана новая плазменно-управляемая технология для предотвращения распространения огня и пожарной защиты пористых материалов. Исследования, проведенные на основе термогравиметрического (ТГА) и дифференциального термического (ДТА) анализа, а также дифференциальной сканирующей калориметрии, подтвердили, что предварительная плазмохимическая обработка материала приводит к замедлению химической реакции горения дерева (*Pinus sylvestris*, Болгария; *Pseudotsuga*, Канада).

ПЛАЗМОВО-КЕРОВАНА ТЕХНОЛОГІЯ МОДИФІКАЦІЇ МАТЕРІАЛІВ ДЛЯ ПІДВИЩЕННЯ ВОГНЕСТІЙКОСТІ

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Останнім часом відзначається визначений інтерес до діелектричного бар'єрного розряду в повітрі при атмосферному тиску і кімнатній температурі завдяки зростаючому числу його технологічних прикладень. Розроблена нова плазмово-керована технологія для запобігання поширення вогню і пожежного захисту пористих матеріалів. Дослідження, проведені на основі термогравіметричного (ТГА) і диференціального термічного (ДТА) аналізу, а також диференціальної скануючої калориметрії, підтвердили, що попередня плазмохімічна обробка матеріалу приводить до уповільнення хімічної реакції горіння дерева (*Pinus sylvestris*, Болгарія; *Pseudotsuga*, Канада).