

OPTIMIZED CONDITIONS FOR GRAFT COPOLYMERIZATION OF POLY(ACRYLAMIDE) ONTO RUBBERWOOD FIBRE

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Graft copolymerization of acrylamide (Am) onto rubberwood fibre (RWF) was carried out by free radical initiation. Ceric ammonium nitrate was used as an initiator system. The effects of temperature, dose of initiator, ratio of monomer to fibre, and nitric acid concentration, on the grafting percentage were investigated. The optimum reaction temperature was found to be about 50°C for 4h and with an appropriate ratio of monomer to fibre of 3:1 wt/wt. The optimum concentration of initiator and nitric acid were 0.007 M and 0.2 M, respectively. The polyacrylamide (PAm) homopolymer was removed from the graft copolymer by Soxhlet extraction using distilled water. The pre-treatment RWF before the grafting procedure showed that grafting of acid-treated had a higher efficiency than alkali- treated and untreated RWF. Fourier transform infrared spectroscopy was used to confirm and characterize the PAm-graft-RWF.

Keywords: Rubberwood fibre; Acrylamide; Lignocellulose; Graft copolymerization

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INTRODUCTION

In Southeast Asia, rubberwood (*Hevea brasiliensis*) is a type of wood taken from the Pará rubber tree, often called the rubber tree. It is valued for its dense grain, minimal shrinkage, attractive colour, and acceptance of different finishes (Hashim et al. 2005). Rubberwood fibre (RWF) is a natural composite material that has gained special importance because it is cheap and plentiful. Rubberwood with its structural chemical characteristics provides desirable properties for many end-use products. Its lignocellulosic nature, consisting of flexible cellulose fibres assembled in an amorphous matrix of lignin and hemicellulosic polymers, makes it a superior material in many applications. Chemical compositions of this wood show that its main components are polysaccharides (67.0%) and lignin (26.0%) (Abu-Ilaiwi et al. 2004).

The cellulose fibre of rubberwood is a non-branched polymer of (1→4) β-O-glucopyranose linkages between glucose units. Most of the cell wall cellulose is crystalline. Cellulosic materials are the most abundant resource in nature and they also can be used as a bioaffinity carrier, and they exhibit good chemical stability, mechanical strength, renewable, high reproducibility, and low cost (Sokker 2006). Cellulose and its derivatives also have been used in metal ion adsorption. Lignin is a three-dimensional phenylpropanol polymer and constitutes 23% to 30% of the wood substance in softwoods and 16% to 22% in hardwoods (Bledzki and Gassan 1996).

The term reactive fibres can be used to denote natural polymers that are used in the selective extraction of metals from aqueous solutions. The fibrous adsorbents, which have large specific surface areas and high adsorption rates, are increasingly used in removal of toxic metal ions and enrichment recovery of traces of elements from aqueous solution. Fibre, in comparison with other available adsorbents, is an excellent cost-effective material (O'Connell et al. 2008). The adsorption of heavy metal ions from aqueous solution by adsorbents is usually controlled by the properties of the surface functional groups of the adsorbents (Sengil and Ozacar 2009).

However native RWF generally have quite low carboxyl and other functional groups compared to what would be most suitable for metal chelating capability. Hence, the fibre has to be functionalized by appropriate chelating functional groups before it can be used effectively to adsorb and hold onto relatively high amounts of heavy metal ions. The properties of fibre may be modified and improved by both physical and chemical methods. Modification of cellulose by graft copolymerization techniques allows one to chemically change the cellulose chain by introducing polymeric chains that confer different structural characteristics to the initial material, which has led to new cellulosic products with improved or new properties (Abu-Ilaiwi et al. 2004).

Grafting of desired functional group-containing chains onto a fibre surface can provide a larger number of functional groups and structures (Kamel et al. 2006). In addition, grafting improves the adsorption capacity and selectivity of fibre significantly by forming many reactive groups upon the polymer chains. Graft copolymerization is a process in which side chain grafts are covalently attached to a main chain of a polymer backbone to form a branched copolymer (O'Connell et al. 2008).

Recently, graft copolymerization of different monomers onto lignocellulosic materials has been used to enhance their properties, for example, grafting of acrylonitrile onto pineapple leaf fibers to improve their thermal properties (Mohanty et al. 2000), acrylamide onto banana stalk to produce a selective adsorbent of Co(II) (Shibi and Anirudhan 2005), acrylic acid onto wood pulp for removing Fe(III), Cr(III), Pb(II), and Cd (II) from aqueous solutions (Abdel-Aal et al. 2006), sunflower stalks with acrylonitrile to remove Cu(II) (Hashem, 2006), acrylamide onto sisal fibers to improve their moisture absorption (Rupali and Premamoy 1999), methyl methacrylate onto jute fibers to enhance their mechanical properties (Khan et al. 2002), and acrylonitrile onto coir fibers which improved their mechanical strength (Rout et al. 2002).

Acrylamide is a polyfunctional molecule that contains a vinylic carbon-carbon double bond and an amide group. The electron-deficient double bond of acrylamide is susceptible to a wide range of chemical reactions including nucleophilic additions, Diels-Alder, and free radical reactions. Acrylamide is also capable of coordinating with less acidic metal ions through the carbonyl oxygen atom and/or the nitrogen atom (Girma et al. 2005). It could be a neutral or negatively charged ligand acting as a monodentate or bidentate chelating ligand to one metal or bridging ligand to two or three metals. The aim of this study was to optimize the graft copolymerization of acrylamide onto RWF. The effect of the reaction parameters on the percentage of grafting was studied. The use of Fourier transform infrared spectroscopy (FTIR) spectroscopy to follow the functional group of the grafted RWF was also investigated.

EXPERIMENTAL

Materials

Rubberwood fibre (RWF) was kindly supplied by Merbok MDF Sdn. Bhd. Kedah, Malaysia with an average length of 2.36 mm. The RWF was first washed with hot distilled water and then with acetone several times to remove dust and any other impurities from the fibre. Acrylamide (Am) monomer and ceric ammonium nitrate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, were purchased from Fluka, China. Acetone and nitric acid were obtained from BDH, UK, and all the chemical used were analytical grade.

Graft Copolymerization of Acrylamide onto RWF

Before the grafting process, the RWF was treated with 1% sulphuric acid for 2 hours or with 1.5% alkali soda for 1 hour under reflux and air-dried. After these processes, the grafting of treated rubberwood has a higher efficiency than the untreated rubberwood fibre. Grafting was carried out by adding 5 g of RWF (w) to distilled water (80 mL) and mixing with a specified amount of ceric ammonium nitrate (initiator) dissolved in nitric acid for 10 minutes in order to create radical sites on the surface of the fibre. To start the copolymerization reaction, solutions of a specified amount of acrylamide monomer in 50 mL of distilled water were added. The mixture was stirred at selected temperatures in a water bath for 4 hours. After grafting, the sample was filtered, washed with distilled water several times, and then air-dried (w_1). Finally, this dried sample was extracted with distilled water in a soxhlet apparatus for 48 hours to dissolve the formed homopolymer. After extraction, the sample was washed with distilled water to remove impurities and air-dried (w_2).

Characterization of PAm-graft-RWF

The change in chemical structure of rubberwood fibre as a result of graft copolymerization with an acrylamide monomer and functionalization was characterized using Fourier transform infrared spectroscopy (FTIR) spectroscopy. The infrared spectra of the polymer was recorded by a model 100 series FTIR spectrophotometer using the universal ATR sampling accessory technique in the range $280\text{-}4000\text{ cm}^{-1}$.

Determination of Grafting Level

The percentage of graft and grafting efficiency were calculated as follows:

$$\text{Graft \%} = [(w_2 - w) / w] \times 100 \quad (1)$$

$$\text{Grafting efficiency \%} = [(w_2 - w) / (w_1 - w)] \times 100 \quad (2)$$

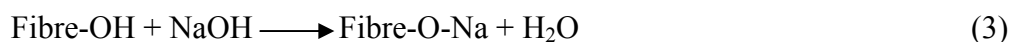
RESULTS AND DISCUSSION

Treatment of Rubberwood

Before the grafting procedure, the rubberwood fibre was pretreated with 1% sulphuric acid for 2 hours or with 1.5% alkali soda for 1 hour under reflux. Of these processes, the grafting of treated rubberwood with acid had a higher efficiency than the

alkali- or untreated rubberwood. This indicates that acid treatment causes a decrease in the degree of polymerization, and consequently the end groups of cellulose fibre chains, causing an increase in the reactivity of the rubberwood to grafting.

In addition, the grafting efficiency of alkali-treated rubberwood was higher than untreated rubberwood. This is because of the increase in the diffusion rate of grafting chemicals through the cellulose chains due to the reduction in the crystalline parts of the alkali-treated rubberwood (Nada et al. 2003). The alkaline treatment promotes the removal of partially amorphous constituents such as hemicelluloses, lignin, and oil soluble in alkaline solution and therefore reduces the level of fibre aggregation, making a surface rougher (Carvalho et al. 2010). During the alkaline treatment, the OH groups present in the fibres react with sodium hydroxide according to Equation (3):



Mechanism of Graft Copolymerization

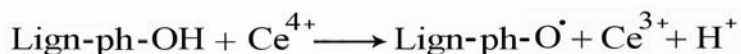
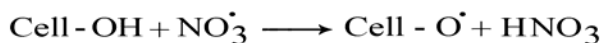
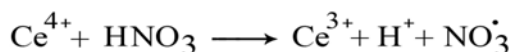
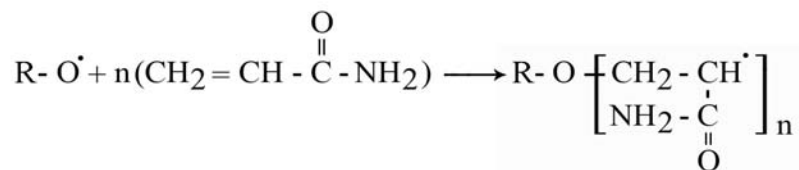
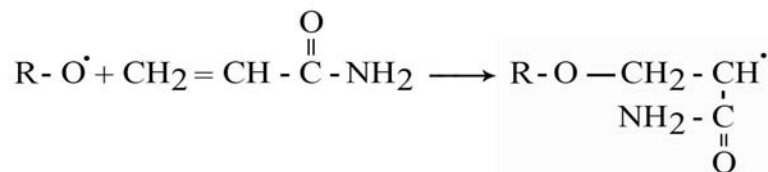
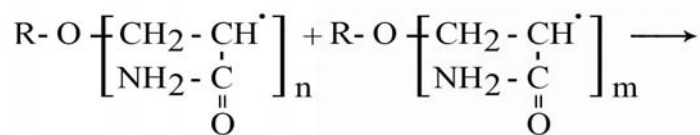
During the copolymerisation, the radical formation for the initiation reaction can occur either on the polymer backbone or on the monomer to be grafted. In the presence of an acrylamide monomer, the fibre macroradical is added to the double bond of acrylamide, resulting in a covalent bond formation between the monomer and the fibre with the creation of a free radical on the monomer, that is, a chain is initiated. Subsequent addition of monomer molecules to the initiated chain propagates grafting onto the fibre (Bhattacharya and Misra 2004).

Therefore the free radical reaction mechanism can be divided into three stages: initiation, chain propagation, and chain termination (Scheme 1).

- Initiation is the creation of free radicals that are necessary for propagation. The products formed are unstable and easily break down into two radicals.
- Propagation is the rapid reaction of these radicalised molecules with another monomer.
- Termination is the coupling of two radical species reacting with each other to form a single molecule.

FT-IR Spectroscopy

Infrared spectra of RWF and grafted RWF are shown in Fig 1. The absorption bands found at 1600 to 1400 cm^{-1} for RWF indicate the presence of aromatic or benzene rings in lignin. The presence of the peak at 1736 cm^{-1} in the RWF spectrum could be due to the carbonyl (C=O) stretching vibration of the carboxyl groups of hemicellulose and lignin in the RWF. Compared with the ungrafted RWF (Fig 1a), a sharp peak appeared in PAm-g-RWF at 1650 cm^{-1} (Fig 1b), corresponding to the stretching of the carbonyl (C=O) of the amide group in acrylamide. In addition, for the grafted polymer a new band at 828 cm^{-1} was also observed, which indicates the (C-H) stretching vibrations in the polyacrylamide molecule. The ratio of the band intensity at 1650 cm^{-1} to the band intensity at 1215 cm^{-1} increased by grafting due to incorporation of CONH₂ groups on the fibre. Both IR spectra of the ungrafted and the grafted RWF exhibited broad adsorption band at 3400 cm^{-1} due to hydroxyl group stretching vibrations from the RWF structure.

Initiation:**Propagation:****Termination:****Grafted copolymer**

Scheme 1. Proposed mechanism of graft copolymerization of Am onto RWF using $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$ as initiator (Cell-OH is a cellulose hydroxyl group, where Lign-ph OH is a phenolic hydroxyl group of lignin, and R-OH is RWF)

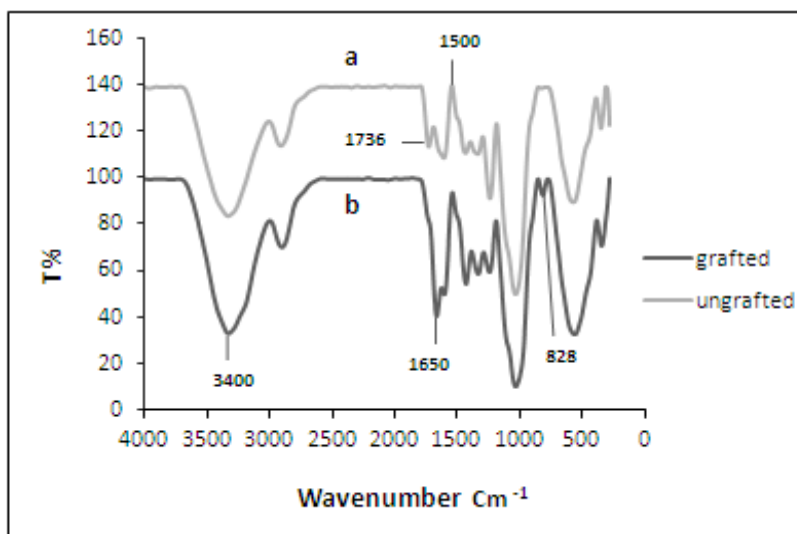


Fig. 1. Infrared spectra of (a) RWF and (b) PAm-g-RWF

Scanning Electron Microscopy

Graft polymerisation has been recognized as a simple and effective technique for introducing large quantities of desirable functional groups into a host substrate; meanwhile, by using this approach, the surface area of RWF can be dramatically increased. Figures 2 and 3 show the changes on the surface area of fibers before and after grafting. Dramatic differences can be easily observed on the surfaces of the untreated and grafted fibers. Unlike the untreated fiber, the surfaces of the grafted fibers seem to be free of surface holes and grooves. This also shows that a considerable amount of PAm was grafted onto the RWF surface. As the surface was covered with grafted polymer, it became more uniform and smooth.



Fig. 2. Scanning electron micrographs of unmodified RWF

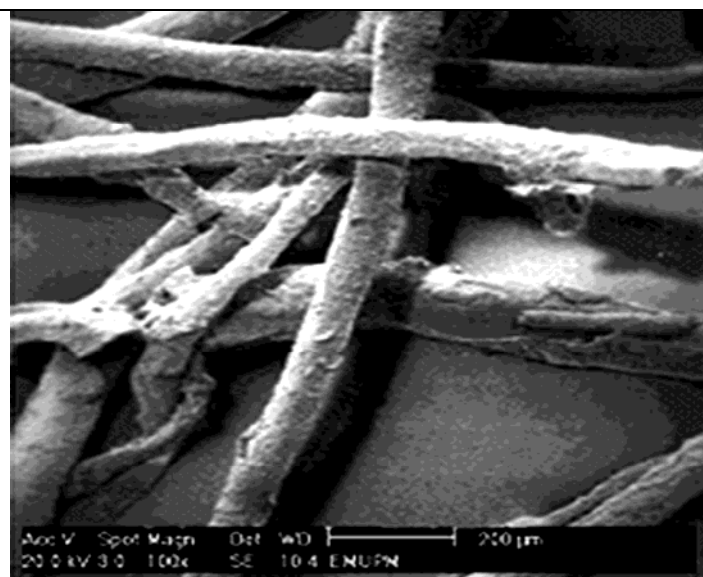


Fig. 3. Scanning electron micrographs of PAm-g-RWF

Effect of Initiator Concentration

The variation on the grafting parameters with ceric ion concentration (initiator) from 1.45×10^{-3} to 2.9×10^{-2} M is shown in Fig. 4. Results show an initial increase in grafting with an increase in the initiator concentration. The highest percentage of graft (98%) and grafting efficiency (52%) were obtained at a ceric ion concentration of 0.007 M. Increasing the initiator concentration more than 0.007 M decreased these parameters. The enhancement of grafting by increasing the ceric ammonium nitrate amount signifies the necessity of a certain amount of initiator on the rubberwood fibre, because initiator produces fibre macroradicals capable for initiating grafting. Thus, results from this study suggest that only a small proportion of ceric ions are consumed in the oxidative reaction of the backbone polymer. The increase of initiator to more than 0.007 M caused a retardation of monomer diffusion through the polymeric chains, accelerating the rate of termination. Alternatively, an increase in the initiator leads to initiation of many chains, which enhances the chance of mutual initiation of growing polymeric chains. These factors cause enhancement in the rate of the formation of homopolymers and a decrease in graft yield (Sikdar et al. 2003).

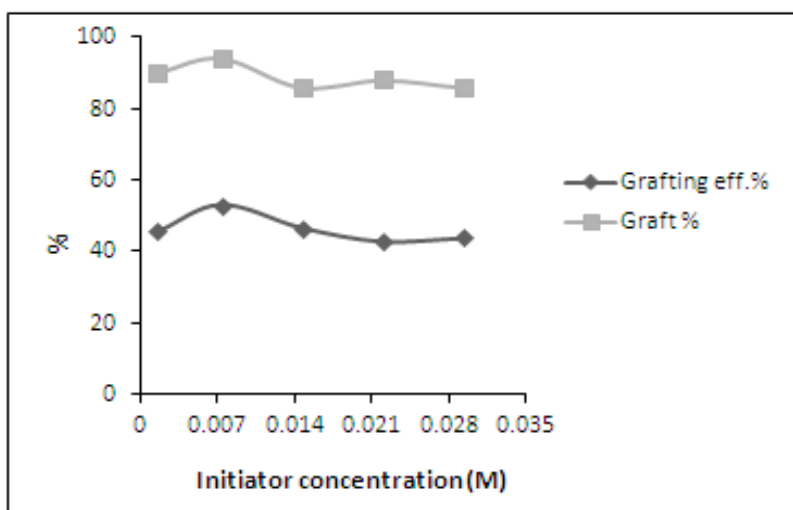


Fig. 4. Effect of initiator concentration on grafting. Reaction conditions: RWF, 5.0 g; acid conc, 0.2 M; Temp, 50 °C for 4h; monomer to fibre ratio 3:1 (wt/wt)

Effect of Nitric Acid Concentration

The effect of nitric acid concentration on the grafting process is shown in Fig. 5. The graft efficiency was increased by increasing the acid concentration from 0.01 to 0.2 M. This behaviour indicates that nitric acid in the grafting medium assists the grafting by causing inter- and intra-crystalline swelling of cellulose, leading to an improvement in monomer accessibility. In addition, 0.2 M acid concentration is satisfactory to create a balance between the control of the rate of the active species formation and the rate of primary radicals. The decrease in the grafting parameters above this concentration could be due to (1) the increase in the coagulation of a colloidal homopolymer at a lower pH (Deo and Gotmare 1999), and, (2) the increase in the oxidation of the formed free radicals, which decreases the rate of initiation with an increase of homopolymer formation.

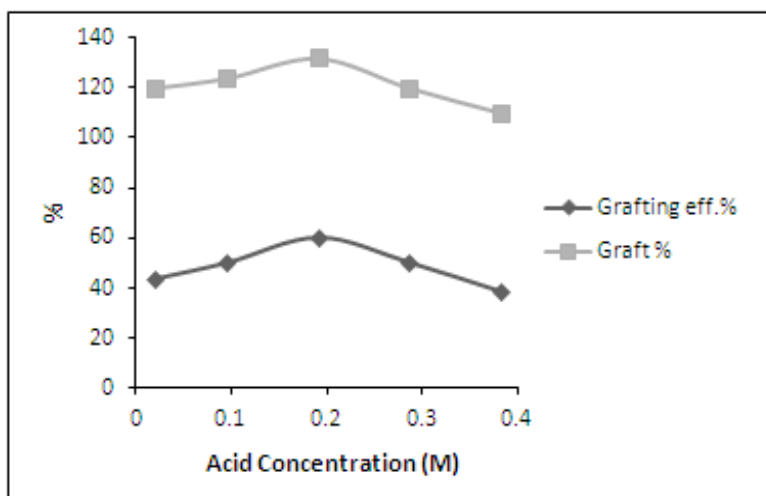


Fig. 5. Effect of acid concentration on the grafting. Reaction conditions: RWF, 5.0 g; initiator conc, 0.007 M; Temp; 50 °C for 4h; monomer to fibre ratio 3:1 (wt/wt)

Effect of Ratio of Monomer to Fibre

The effect of ratio of the amount of acrylamide to RWF on the grafting parameters is shown in Fig. 6. It is clear from the figure that the percentage of graft and graft efficiency increased with the increase of monomer concentration, and remained constant after a 3:1 ratio of monomer to fibre using a constant initiator concentration of 0.007 M.

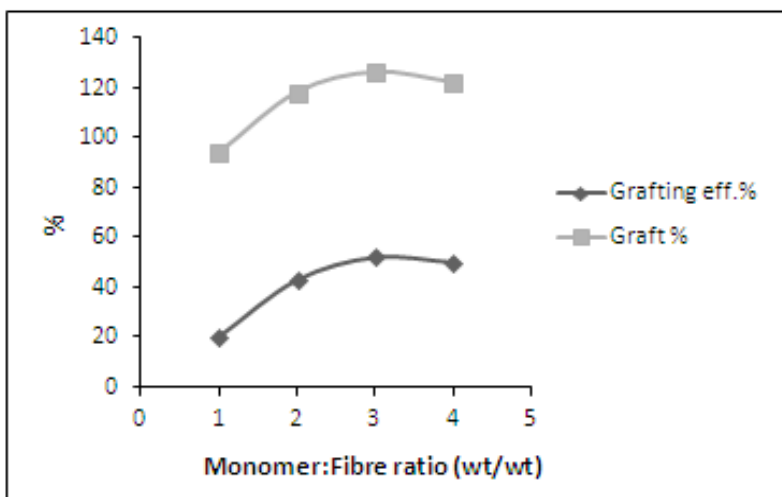


Fig. 6. Effect of monomer to fibre ratio on the grafting. Reaction conditions: RWF; 5.0 g, initiator conc; 0.007M, acid conc; 0.2 M, Temp; 50 °C for 4h

Enhancement in grafting percentage can be explained by the higher availability of acrylamide monomer molecules around the fibre macroradicals, which is a prerequisite for graft initiation and propagation. Fibre macroradicals are relatively immobile, and so for grafting to occur, the monomer molecules need to be in close proximity to those fibre macroradicals. Thus, the enhancement may be due to the formation of long graft chains. On the other hand, the maximum amount of acrylamide monomer that can be complexed

will be fixed. An increase in monomer concentration above the maximum value would not be expected to lead to an increase in grafting parameters (Okieimen 2003).

Effect of Reaction Temperature

Graft copolymerisation of acrylamide onto RWF was carried out from 27 to 70°C, and the results are shown in Fig. 7. The increase in grafting parameters with increasing reaction temperature from 27 to 50°C could be due to (1) better decomposition of the redox system, giving rise to more free radicals, (2) enhancement in the mobility of the monomer molecules and their collision with backbone macroradicals, (3) the increase in the rate of diffusion of monomers to polymeric chains, and (4) a higher rate of initiation and propagation of the graft chain.

On the other hand, the decrease in the grafting percentage with an increase in reaction temperature above 50°C could be attributed to the increase in the rate of radical termination and the formation of homopolymer chains (Abu-Ilaiwi et al. 2003).

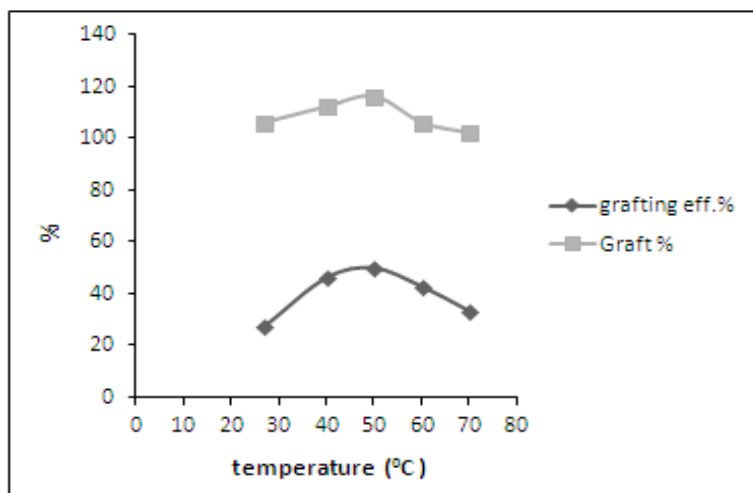


Fig. 7. Effect of reaction temperature on the grafting. Reaction conditions: RWF; 5.0 g, initiator conc; 0.007M, acid conc; 0.2 M; monomer to fibre ratio 3:1 (wt/wt)

CONCLUSIONS

1. Graft copolymerization of acrylamide onto rubberwood fibre was successfully carried out by using ceric ammonium nitrate as an initiator system.
2. The optimum conditions of graft copolymerization were an initiator concentration of 0.007 M, an acid concentration of 0.2 M, a reaction temperature of 50°C, and a ratio of monomer to rubberwood of 3:1(wt/wt) for 4 hours.
3. The presence of polyacrylamide on the grafted product was indicated by FT-IR spectroscopy.

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