Supplementary Information

PMMA-g-SOY as a Sustainable Novel Green Dielectric Material

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Characterization

The surface morphology of pristine and copolymer samples were imaged by scanning electron microscopy (SEM) using a Hitachi S-2460N variable pressure SEM (VP-SEM) under 60–80 Pa of helium atmosphere. The SEM images were collected using the backscattered electron signal at an accelerating voltage of 20 kV and from a working distance of 25 mm.

Optimization of different reaction conditions for maximum percentage of grafting

Optimization of various reaction parameters for maximum percentage graft copolymerization of MMA onto SOY (Figures S1-S5). Figures S6, SEM analysis of fracture surfaces of the pristine PMMA and PMMA - g – SOY

Effect of Solvent

The degree of grafting as a function of solvent (water) is seen in Figure S1. It shows that maximum grafting is reached in 20 mL solvent and then decreases with further increase in the amount of solvent.



Figure S1 Degree of grafting as a function of solvent (water)

This can be explained by the fact that higher amounts of water may inhibit the interaction between reaction components (soy flour backbone and graft chains), which led to a lower grafting yield ³⁰

Effect of Reaction Period

The degree of grafting as a function of reaction time is shown in Figure S2. The degree of grafting increased when reaction time increased from 120 to 300 minutes, while further increase in reaction time above 300 minutes resulted in a decrease in the degree of grafting. The initial increase may have been caused by increased interactions of the primary free radicals with the monomer and the SOY, resulting in the generation of more free radical sites and therefore a higher degree of grafting³⁰. However, after reaching an optimum polymerization degree, further increase in reaction time suppressed graft copolymerization because of the increase in induced initiator decomposition and reduced availability of radical sites on the SOY back bone caused by an abstraction process.



Figure S2 Degree of grafting as a function of reaction time

Effect of Reaction Temperature

Figure S3 shows the effect of reaction temperature on graft copolymerization while all other parameters were kept constant. With increasing reaction temperature, the degree of grafting increased until 60 °C was reached; further increases in reaction temperature resulted in a decreased degree of grafting. This effect may be attributed to the fact that at low temperatures the reaction between SOY and APS initiators as well as the decomposition rate of the initiators is slow. With increasing temperature, the reaction was accelerated with the increasing level of kinetic energy, resulting in more free radicals and thus a higher rate of graft copolymerization. ³⁰



Figure S3 Effect of reaction temperature on graft copolymerization

However, once the temperature passed the threshold of 60 °C, the degree of grafting slightly decreased because now homo-polymerization of the MMA monomer dominated the graft copolymerization reactions.

Effect of Initiator Concentration

Graft copolymerization onto SOY was carried out using ammonium persulphate (APS), a water-soluble initiator. The degree of grafting increased with an increase in initiator concentration from 11 mmol/ L to 44 mmol/ L; further increase in initiator concentration decreased the degree of grafting (Figure S4). The initial increase in degree of grafting was attributed to the increase in number of the SO_4 -* free radicals. These primary free radicals generated more free radical sites on the SOY backbone and on the MMA monomer. However, with further increases in initiator concentration beyond 44 mmol/ L, the free radicals that initiate grafting onto the SOY backbone were saturated and extra free radicals initiated the homo-polymerization of MMA and led to a lower degree of grafting.



Figure S4 Effect of initiator concentration on degree of graft copolymerization

Effect of Monomer Concentration

The effect of different concentrations of methyl methacrylate (MMA) monomer in the reaction mixture on the graft copolymerization of SOY was studied (Figure S5). The degree of grafting onto SOY increased with the addition of a small amount of MMA to the reaction mixture. With 0.97 mol/ L of MMA the degree of grafting reached a maximum of 127 % under optimum conditions, beyond which it decreased. Graft copolymerization onto soy depends not only on monomer concentration but also on other factors, such as the number of reactive sites along the soy main chains and steric effects that inhibit grafting. With monomer concentration increasing beyond the optimum value, most reactive sites were already reacted and no longer available for further grafting so that increasing monomer concentration resulted in the homo-polymerization of monomer MMA ^{31, 32}.



Figure S 5 Effect of monomer concentration on degree of graft copolymerization



Figures S6 FTIR of pristine SOY and PMMA - g - SOY with different percentage of grafting.



Figures S7 TGA/DTG of PMMA - g – SOY with 33.4 % percentage of grafting.



Figures S8 TGA/DTG of PMMA - g - SOY with 56 % percentage of grafting.



Figures S9 TGA/DTG of PMMA - g – SOY with 75 % percentage of grafting.



Figures S10 TGA/DTG of PMMA - g – SOY with 91 % percentage of grafting.