ORIGINAL ARTICLE

JanusStudy on Surface Modification of particles and their Compatibilizing properties to blend Polymers

Yuxin Liu

Institute of Architectural Engineering, Shijiazhuang, Hebei Province, 050000

Abstract: In this paper, the snowmanSio_2@ Pdvb JanusParticles as template,Through surface modification, different surface propertiesJanusParticle,Included inSio_2Introduction of Polybutadiene into the hemisphere(PBD)With polyisoprene(PI),To increaseSio_2@ Pdvb JanusInorganic in particlesSio_2Hemispheric affinity for Polymer Matrix.Will then be modified before and afterJanusParticles dispersed into Polystyrene(PS)/Butadiene Rubber(PBD)And Polystyrene(PS)/Isoprene rubber(PI)In the blend system,Inspected the differentJanusEFFECT OF PARTICLES ON PHASE STRUCTURE OF BLENDS.Found the result,With unmodifiedJanusParticle comparison,Introduction of polymer brushJanusParticles can improve the interface Compatibilizing Effect more effectively,Kinetics of inhibiting PHASE SEPARATION OF BLENDS.

Keywords: JanusParticle,Surface Modification,Zengrong,Polymer Blends

1. Introduction

JanusParticle is a class surface at the same time has two kind of different chemical composition and strict partition of new particles[1 ~ 4]In Solid Emulsifier, interface capacity, interface catalytic, function coating, cells diagnosis and treatment and field the important of Research Progress[5 ~ 9].As an interface compatibilizerJanusParticle unique of structure characteristics make its both surface active agent of parents of and solid particlePickeringEffectThan homogeneous nano-particle or block copolymer has stronger of stable interface roleIn polymer blend of in show excellent of capacityIs expected to become a new generation of capacity Agent[10]. China Academy of Sciences chemical Institute Guo red researcher Research Group[11,12]Simulation.JanusParticle on don't compatible blend polymer phase separation behavior

InfluenceResults show thatAnd homogeneous particle comparedJanusParticle can more effective to suppression phase area of growthReduce phase area of size.Experimental study also show that[13]InJanusParticle of different surface intervalRespectively introduced and blend polymer chemical properties phase matching of polymer brushCan significantly improveJanusParticle in polymer phase interface of aggregation behavior.In additionPolymer brush and blend polymer molecular of each other DiffusionAlso can suppression for system conformation entropy loss of Surface Energy ChangeEnhanced particle in interface of stability. M u llerSuch.[14,15]Preparation the with Polystyrene (PS) And poly (methyl metha cry late) (PMMA) Molecular brush Janus Particle Observe the ITS on PS/PMMA Blend System of capacity Effect Found even if high mild high shear role underParticle can still stability to aggregation in InterfaceShow excellent of Interface Activity and Capacitive.Hangzhou Normal University Lee Yong Jin Professor Research

Group[16,17]Use block copolymer in Situ Polymerization MethodsPreparation the with ju jia ji bing xi

2. Experimental part

2.1 Main raw materials

ButadienePolymerization levelOf Qilu Petrochemical(, China);IsoprenePolymerization Shandong huaju polymer material limited the company(, China); SiO_2@ PDVB JanusMicrospheresDongying Janus New Materials Science and Technology Limited the company(, China);N-BuLi2.5 mol/L,Dispersion in CyclohexaneAladdin Reagent(, China);Chlorine ethyl trimethoxysilane 99%, Aladdin Reagent;Triethylamine99%,Aladdin Reagent;PolystyreneMW = 270 K,Aladdin Reagent;Isoprene rubber(PI),M_W= 610 K;Butadiene RubberBR9000 (PBD),MW = 500 k,Purchase self-Qingdao yi ke si New Enterprise(, China);CyclohexanePureTianjin Boddy chemical shares limited the company(, China),"With before the refinedSpecific for will be the right amount of sodium and benzophenone join to cyclohexane add heat refluxStay solution into dark blueWill cyclohexane DistillationCollection spare.DichloromethanePureTianjin Fu Yu fine chemical limited the company(, China);ToluenePureLaiyang Economic Development Zone fine Factory(, China).

2.2 Experimental steps

2.2.1 Snowman-Sio_2@ PDVB JanusParticle of surface modified

As shown in figure1Shown inBy grafting to the methods will Polybutadiene(PBD)Or polyisoprene(PI)Molecular link branch to inorganicSio_2Hemisphere SurfaceTo

2.2.3 Macromolecules silane coupling agent of preparation

To2.2.2Section in complete the preparation of with activity center of Polybutadiene cyclohexane solution inJoin2 mLChlorine ethyl trimethoxysilaneReaction temperature25 ℃ Reaction Time12 h,In the molecular chain of end introduced silane coupling agent.The product rotating evaporation afterIn45℃ Vacuum drying oven in dry to constant weightReady to next step reaction.

2.2.4 PBD-SiO_2@ PDVBOf Synthesis

Will0.5gOfSio_2@ PDVB JanusParticle Dispersion in toluene solution inJoin2.2.3Section in preparation1g Macromolecules silane coupling agent and0.5 mlOf triethy lamine Solution Reaction temperature25℃Reaction Time24 h,With dichloromethane cleaning ParticleUntil the supernatant in detection can't the Molecular Chain.Macromolecular coupling agent at the end of the methoxy andSio_2@ PDVB JanusParticle inSio_2Hemisphere surface of hydroxyl ReactionWill the molecular link branch to silica sidePolymer brush modifiedJanusParticle(PBD-SiO_2@ PDVB),Can observe the to particle was viscous state.

PI-SiO_2@ PDVBAndPBD-SiO_2@ PDVB JanusParticle of preparation

Methods The sameJust will butadiene into IsoprenePolybutadiene become polyisoprene.

2.3 Test Characterization

AdoptedBruker (500 MHz,Germany)Analysis of microstructure of polymer brush by NMR,Samples were treated with deuterated chloroform at room temperature(Han1% TMS)Dissolve, Formulated 2.W/V% Solution. Adopted Jem2100 Transmission Electron Microscopy(TEM,Japan)ObservationJanusMorphology of Particles,Operating voltage is200 kV.Phase Morphology of the blends was characterized by OlympusBx51Phase contrast microscope (Japan) Observation.Blend Membrane placement150Phase Morphology After annealing at different temperatures.Molecular Weight and distributionHLC-8320Gel permeation chromatograph Test,Using tetrahydrofuran as mobile phase,Using monodisperse polystyrene as standard sample.Column temperature30C,The differential temperature detector is35C,Flow rate of mobile phase1.0 mL/min,The injection amount is50 µL.Adopted modelTg209f1libra (netzsch,Germany)The thermal weight loss Instrument Analysis polymer of graft DensityTo10℃/MinThe heating rate will samples from room temperature900℃Graft Density Calculation Formula[20]Are as follows:

WhichG_RRepresentative weight graft DensityW_1Representative not graftJanusParticle in thermal weight loss instrument heating900 ℃ After the residual inorganic contentW_2Representative graftJanusParticle in thermal weight loss instrument heating900℃ After the residual inorganic content.

3. Results and discussion

3.1 Silane coupling agent graftPBDOf Hydrogen Spectrum Analysis

Figure2For silane coupling agent graft the molecular chain^{1}H NMRSpectrum figure.The Representative PBD Molecular Chain cis-1,4-Double Bond on the hydrogenA1Peak very obviousRepresentative1,2-Structure of side chain on the double bond on the hydrogenA2Is weakA3Ownership for methoxy-OCH3Hydrogen atom of chemical displacement Methoxy hydrogen atom of chemical displacement of proof of the existence silane coupling agent graft shang ju

Butadiene Molecular Chain.By calculationThe Molecular Chain high cis-1,4-StructureIts1,4-Structure accounted93 mol % 1,2-Structure accounted7/mol %[21].

3.2 PI-SiO_2@ PDVBThe thermal weight loss Study

Figure3Given the modified before and after two of particle of thermal weight loss curveBecause polymer brush the introductionModified after inorganicSio_2Of solid content was significantly lower than that of the modified before Janus Particle.By calculationPI-SiO_2@PDVB Of Quality graft density47.8 wt %.The other by test Graft PBD,PI Molecular brush of molecular weight respectively 64 K,114 K,Dispersion Coefficient respectively 1.4,1.3.

3.3 Sio_2@ PDVBModified before and after of morphology

PDVBSide for hollow structureAnd present mesoporous structureHead of silica was smooth state. PDVB Hemisphere in NN-Dimethylformamide (DMF) Etching before PDVB-PS Complex DMF Etching out linearPSMolecular Chain afterIn cross-linkingPDVBHemisphere left mesoporous structure.Figure4 (B) ForSio_2 Hemisphere graftPBDAfterSio_2@ PDVB JanusParticle Morphology.When PBD Molecular link branch in silica hemisphere when Original smooth of surface can observe the to obvious of polymer layer With the solvent of volatile Graft polymer molecular brush of side each other closeSelf-assembly formation superstructure(1-3),On both sides of the opposite sexJanusParticle the reason has two pro-Self-assembly is one of the important of Factors[22,23].

3.4 PBD-SiO_2@ PDVBCapacityPS/PBDBlend System of Research

PS/PBDFor don't compatible blend systemIn spin-coating of process inDue to solvent of Induced by role[24]PS/PBDBlend of presents obvious of Two-Phase Structure(Figure5),In add different contentPBD-SiO_2@ PDVB JanusParticle afterCan found phase structure with changePhase area size slightly smallerAt the same time High Concentration Particle inPS/PBDBlend of in the obvious of aggregation Phenomenon(Figure5 (c d)).Figure6ForPS/PBDBlend of in150 ℃ Annealing processing2 hAfterDifferent ConcentrationPBD-SiO_2@ PDVB Ja-nusParticle of Phase Morphology of influence.

ObviouslyAnd annealing before comparedPS/PBDBlend of the two-phase structure more obviousJoin particle afterPS/PBDBlend of phase area size significantly reduceAnd particle content the higherPhase area size the small.When particle content increase15%An arcanePSAndPBDOf double Continuous Phase StructureBut not deny15 wt %High ContentPBD-SiO_2@ PDVB JanusParticle inPS/PBDBlend of in same accumulation wasThis is due to the particle of decreased the polymer molecular chain of conformation entropyWhen particle concentration increase to a certain degree afterSystem entropy loss too much and can't make particle stability in polymer inParticle aggregate becomes obviousAnd from polymer phase separation..

Figure7/For don't add or add differentJanusParticlePS/PBDBlend System in150 ℃ Annealing2 hAfter the Phase Morphology.ObviouslySolid Particle of join can be effective regulation blend polymer of Phase Structure.And not modifiedSio_2@ PDVB JanusParticle comparedModified afterPBD-SiO_2@ PDVB JanusSolid Particle capacity effect more obvious.This is because modified

Former, SiO_2.@ Pdvb JanusIn ParticlesPdvbWithPSGood affinity,Particles are more pronePSPhase dispersion,After modification,Grafting onSio_2.HemispherePBDMolecular Chain and blend Polymer MatrixPBDGood affinity,To a certain extent, the balanceJanusAffinity of particles to two-phase Blends,Enhanced interfacial activity and inhibition of phase separation kinetics of blend Polymers,As shown in Fig.7 (c)Shown, PS/PBDBlend polymer with smaller phase size.

Figure8.UnadornedSio_2.@ Pdvb JanusParticle pairPS/PIEFFECT OF PHASE MORPHOLOGY OF BLENDS.You can see,Lower5 wt %ContentSio_2.@ Pdvb JanusParticle pairPS/PIThe increase in capacity is not obvious,High ContentSio_2.@ Pdvb JanusDispersion of particles in blends becomes difficult,The reunion of particles becomes serious..This is due to unmodified before,Solid Particle PairsP SShow a strong affinity,Interface Activity?

Connecting two phases mainly by physical adsorption,So the effect is not?

3.5 Pi-SiO_2.@ PdvbZengrongPS/PIStudy on Blending System

Using the same Synthesis Method,Poly Isoprene(PI)GraftedSio_2.@ Pdvb On Particle,Synthesized PiSolid Particles of Molecular Chain, Pi-SiO_2.@ Pdvb.Will Pi-SiO_2.@ Pdvb Janus Particles added PS/PI (6/4 wt %/wt %) After blending,Rotating Coating,And Yu150Annealing100 min,ObservationPi-SiO_2.@ PdvbOkay.PS/PI Blending

The role of the system.

Solid Particles grafted onto poly is oprene Molecular ChainP I-SIO_2.@ Pdvb, FillPS/IRAfter blending, In150Annealing 100 min After the Phase Morphology As shown in figure 9 Shown in.Can see Modified after the solid particle fillPS/PIBlend System inNo serious of reunion Phenomenon. PS/PIBlend of performance for obvious of Two-Phase StructureAnd with the particle content of increasePhase structure of characteristics size reduceAnd not modifiedSio_2@ PDVB JanusParticle differentPIMolecular Chain inSio_2Hemisphere the introductionReduce the

Mixed of interface tension And very well balanceSio_2Hemisphere and PDVB Hemisphere and PI And PS Back ground of affinity To the better of capacity Effect.

Figure10For5%ContentSio_2@ PDVBAndPI-SiO_2@ PDVB JanusParticle inPS/PIBlend of in Distribution.Can seeSio_2@ PDVB Janus Particle reunion is obvious And main agg regation in PS Phase Modified afterPI-SiO_2@ PDVB JanusParticle although dispersion is not modified before goodBut also most aggregation inPSPhaseThis may is by snowman-Sio_2@ PDVBParticle of Structure DecisionPDVBHemisphere ofPSO Affinity stronger thanPIOf affinity And Sio_2 Hemisphere of area bigSoEven if modified after can appropriate weakenedSio_2@ PDVB JanusParticle on a phase(PS)Of priority wettabilityBut can't makeSio_2.Hemisphere pairPiPerfect affinity and Pdvb Hemisphere pairPSThe affinity against.

4. Conclusion

In this paper, the snowmanSio_2.@ Pdvb JanusParticles as template,Prepared by Anionic Poly merization Pi And PBD Molecular Chain introducedSio_2.Hemisphere, Made upPBD-SiO_2.@ Pdvb janus ParticlePi-SiO_2.@ Pdvb ja-Observation of Compatibilizing Effect,It is found that the introduction has good compatibility with the polymer substrate. Nus Particle.Subsequently,Before and after modificationSio_2.@ Pdvb With PBD-Polymer brush can effectively improve the inter facial Compatibilizing Effect, And then control the Blending

Sio_2.@ Pdvb Janus Particle andPi-SiO_2.@ Pdvb Janus ParticlePHASE STRUCTURE OF POLYMER.This study proves that,2) amphiphilic Janus Grain

IntroducedPS/PBDAndPS/PIIn the blend system,Through the MatrixIt is expected to become an ideal compatibilizer for the next generation.

References

1. Liang F, Liu J, Zhang C, Qu X, Li J, Yang Z.Chem community, 2011, 47: 1231-1233
2. Walther A, Müller Ashe.Chem Rev, 2013,113: 5194-5261
3. Deng R, Liang F, Zhu J, Yang Z.Mater chem front, 2017, 1: 431-443

4. Chen Y Liu twig u & Z By the X Liang F Yang twig u & Z.Chem Asian J2016 11: 1785-1788
5. Yang Q Loos K.Polym Chem2017 8: 641-654
6. Liang F x Yang twig u & Z.ACTA Polym Sin2017 6: 1-10 (. Chinese)[Beam FuxinYang zhen zhong.Polymer Journal2017 6: 1-10]
7. Liu Y Liang F Wang Q By the X Yang twig u & Z.Chem Commun2015 51: 3562-3565
8. [Twig u & Z Liang F Zhang G Ji x Wang Q By the X Song x Yang twig u & Z.Macromolecules2015 48: 3598-3603
9. B Zhu L.Macromolecules2009 42: 9369-9383
10. Liu Z [R Xu G Huang twig u & Z Yan LT.Nano Lett2014 14: 6910-6916
11. Huang M Li twig u & Z [H.Soft Matter2012 8: 6834-6845
12. Huang M [H.Soft Matter2013 9: 7356-7368
13. Nie H Zhang C Liu Y He.Macromolecules2016 49: 2238-2244
14. Bryson kc l o bling ti m u ller AHE Russell TP Hayward RC.Macromolecules2015 48: 4220-4227
15. Bahrami r l o bling TI Gr o schel AH. Realize h m u ller AHE altstädt V.ACS nano2014 8: 10048-10056
16. Wang H Dong W Li Y.ACS Macro Lett2015 4: 1398-1403
17. Wang H Fu twig u & Z Dong W Li Y Li J.J Phys Chem B2016,120: 9240-9252
18. Sun Y Liang F by the X Wang Q Yang twig u & Z.Macromolecules2015 48: 2715-2722
19. Tang C Zhang C sun Y Liang F Wang Q Li J By the X Yang twig u & Z.Macromolecules2012 46: 188-193
20. Perrier S.Macromolecules2006 39: 8603-8608
21. Mao s twig u & Z Wang d h.ACTA Polym Sin1990 2: 111-114 (. Chinese)[Mao JaneKing Edward's.Polymer Journal1990 2: 111-114]